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One-Electron Rotatory Power*

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It is shown that a single electron moving in a field of suitable dissymmetry can give rise to optical rotatory power in a medium containing molecules of this type. This effect is called *one-electron rotatory power* and is in striking contrast to the models developed by Born, Oseen, Gray and others in which a dynamic coupling between several electronic oscillators is responsible for the rotatory power. The detailed calculations are carried out for the potential function,

$$V=\tfrac{1}{2}(k_1x^2+k_2y^2+k_3z^2)+Axyz,$$

which shows rotatory power both quantum mechanically and classically. Next it is shown how fields of this type may be adapted to an approximate description of the field in which the chromophoric electrons of a molecule move, the constants k_1, k_2, k_3 and A being largely determined by the average charge on the different atoms of the molecule as found from additivity of dipole moments due to the bonds in the molecule. As illustrations of the theory absolute calculations are made for the contribution of the nitrite group to the rotatory power of methyl phenyl carbinol nitrite which agrees satisfactorily with experimental data, for the phenyl group contribution of the same molecule and for the hydroxyl group contribution in secondary butyl alcohol. In the latter two instances the theoretical values are much too small but as there is a great deal of freedom in the choice of the configuration because of free rotation these results merely indicate need for more detailed calculations. The general quantum-mechanical theory of circular dichroism is developed and a quantum-mechanical derivation of Natanson's rule is given. The quantum-mechanical definition of Kuhn's "anisotropy factor" is given and an alternative measure of the contribution of an absorption band to rotatory power called the *rotatory strength* is defined and discussed. It is shown that spin magnetic moments may generally be neglected in calculation of rotatory power owing to the weakness of spin-orbit interaction. Interpretation of experiments of Schwab, Rost and Rudolph on the catalytic dehydration of butyl alcohol on active quartz is discussed and kinetic arguments advanced to show how the relative configuration of quartz and butyl alcohol may be inferred from such data. The relation of one-electron rotatory power to known dipole moment and solvent effects on rotatory power is briefly discussed.

I. INTRODUCTION

THE property of some liquids to rotate the plane of polarization of linearly polarized light traversing them has played a great role in the development of stereochemistry. In spite of the fact that an enormous amount of work has been devoted to the subject it cannot be said that the theory of the molecular actions responsible for this behavior is in a very satisfactory state. In this paper we shall attempt to carry the quantum-mechanical treatment of the subject further in terms of a simple model which exhibits the main features of the phenomenon.

By way of review let it be recalled that the rotation is produced as an indirect effect of circular double refraction, that is, because of the medium's having slightly different indices of refraction for right and left circularly polarized light. The rotation is called positive if the plane is turned in a clockwise direction as viewed by an observer into whose eyes the light enters and

* A preliminary account of the main results of this paper was presented at the Denver Meeting of the American Physical Society, June 26, 1937.

the classical analysis due to Fresnel[1] shows that φ, the rotation per unit length of path, is given by

$$\varphi=(\pi/\lambda)(n_l-n_r) \tag{1}$$

in which λ is the vacuum wave-length and n_l, n_r are the refractive indices for left and right circularly polarized light, respectively. On the electromagnetic theory of light circular double refraction can be described phenomenologically by assuming that the medium is characterized by a parameter g defined by the equation

$$\begin{aligned}\mathbf{D}&=\epsilon\mathbf{E}-g\dot{H},\\ \mathbf{B}&=H+g\dot{E},\end{aligned} \tag{2}$$

in which $\mathbf{D}$ and $\mathbf{B}$ are the electric and magnetic inductions and $\mathbf{E}$ and $\mathbf{H}$ the field strengths, ϵ the effective dielectric constant for the frequencies involved, so that ϵ equals the square of the mean refractive index. Then a solution of Maxwell's equations by standard methods gives for the rotatory power

$$\varphi=(2\pi/\lambda)^2cg. \tag{3}$$

The parameter g is the macroscopic representative of a corresponding microscopic parameter representing the response of individual molecules to the applied fields of the light wave. Let $\mathbf{p}_1$ be the induced electric moment of the molecule due to the fields of the light wave and $\mathbf{m}_1$ the corresponding induced magnetic moment. Then we assume that these are of the form

$$\begin{aligned}\mathbf{p}_1&=\alpha\mathbf{E}'-(\beta/c)\dot{H},\\ \mathbf{m}_1&=\quad+(\beta/c)\dot{E}',\end{aligned} \tag{4}$$

where α is the quantity commonly called the polarizability of the molecule, β is a new parameter that is responsible for the optical activity, and $\mathbf{E}'$ is the effective field acting on a molecule. Accepting the Lorentz' result that

$$\mathbf{E}'=\mathbf{E}+4\pi\mathbf{P}/3, \tag{5}$$

where $\mathbf{P}=N_1\mathbf{p}_1$ is the electric moment in unit volume, N_1 being the number of molecules in unit volume, then the standard definitions $\mathbf{D}=\mathbf{E}+4\pi\mathbf{P}$ and $\mathbf{B}=\mathbf{H}+4\pi\mathbf{M}$ lead to the following connections between α and ϵ, and β and g, respectively,

$$\frac{4\pi N_1\alpha}{3}=\frac{\epsilon-1}{\epsilon+2};\quad \frac{4\pi N_1(\beta/c)}{3}=\frac{g}{\epsilon+2}. \tag{6}$$

[1] Fresnel, Ann. chim. phys. **28**, 147 (1825).

The first of these is the familiar result from the ordinary theory of dispersion, the second is its analog for the theory of optical activity. Using the well-known result $n^2=\epsilon$ where n is the mean index of refraction, a combination of (6) and (3) permits the expression of the rotatory power φ in terms of the molecular parameter β and other defined properties of the medium,

$$\varphi=(16\pi^3/\lambda^2)N_1\beta\cdot\tfrac{1}{3}(n^2+2). \tag{7}$$

With this equation the task is completed of expressing the observed rotation per unit length φ in terms of the molecular parameter β, the number of active molecules in unit volume N_1, the vacuum wave-length λ and the mean index of refraction, n. In this way the theory of optical activity is referred back to a molecular theory of β.

Instead of dealing with the rotatory power itself it is often convenient to deal with the molecular rotatory power which is defined as $\varphi M/\rho$ where M is the molecular weight and ρ is the density. Denoting the molecular rotatory power with Φ one has

$$\Phi=(16\pi^3/\lambda^2)N\beta(n^2+2)/3, \tag{8}$$

where N is Avogadro's number. Either (7) or (8) may be used to compute value of β from experimental data on the rotatory power. Unfortunately values of the refractive index are often not given in the literature so the factor $(n^2+2)/3$ has to be estimated.

The appropriate extension of the quantum-mechanical theory of dispersion needed to give the theory of the parameter β has been given by Rosenfeld.[2] Suppose the quantum states of the molecule are labeled by a, b, $\cdots$ where a single letter stands for the totality of quantum numbers needed to specify the state. Then the matrix components of the electric moment of the molecule are denoted by $(a|\mathbf{p}|b)$ and those of magnetic moment by $(a|\mathbf{m}|b)$ where

$$\mathbf{p}=e\sum_i\mathbf{r}_i \qquad \mathbf{m}=\frac{e}{2mc}\sum_i(\mathbf{r}_i\times\mathbf{p}_i+2\mathbf{S}_i), \tag{9}$$

the sum being extended over all the electrons in the molecule, $\mathbf{r}_i$ being position, $\mathbf{p}_i$ momentum

[2] Rosenfeld, Zeits. f. Physik **52**, 161 (1928); see also Condon, "Theories of Optical Rotatory Power," Rev. Mod. Phys. (in press).

and $\mathbf{S}_i$ spin angular momentum of the ith electron. The necessary generalization of the ordinary dispersion theory is obtained by taking into account to the first order the finite ratio of molecular diameter to wave-length of light. The end result of Rosenfeld's calculations is that

$$\beta_a/c=\frac{1}{3\pi h}\sum_b \frac{\mathrm{Im}\{(a|\mathbf{p}|b)\cdot(b|\mathbf{m}|a)\}}{\nu_{ba}^2-\nu^2}, \quad (10)$$

where the expression has been simplified to take account of the fact that the molecules are oriented at random. In this expression ν is the light frequency and ν_{ba} is the frequency associated with a transition from state a to state b. The symbol Im{ } means "imaginary part of" in the sense

$$\mathrm{Im}\{u+iv\}=v \quad (11)$$

if u and v are real. The subscript a on β means that the formula gives the appropriate value of β for molecules in the state a. If in the actual material the molecules are distributed over various initial states such that $N_1(a)$ is the number of molecules in unit volume in the state a then the effective value of β for use in (4) is the weighted average

$$\beta=(1/N_1)\sum_a N_1(a)\beta_a. \quad (12)$$

Equation (10) for (β_a/c) is entirely analogous to the more familiar equation for the ordinary polarizability, α_a,

$$\alpha_a=\frac{2}{3h}\sum_b \frac{\nu_{ba}|(a|\mathbf{p}|b)|^2}{\nu_{ba}^2-\nu^2}. \quad (13)$$

The work of Rosenfeld thus refers the parameter β and hence the optical activity back to the matrix components of electric and magnetic moment as contained in (10). It appears that in all the years since Rosenfeld's paper no attempts have been made to discuss the quantum-mechanical formula (10) in relation to an actual molecular model. Instead there has been a tendency to revert to the original coupled oscillator model of Born,[3] Oseen[4] and Gray[5] in what attempts have been made recently[6–8] to discuss the theory of optical activity. The opinion prevalent in the literature[9] seems to be that the only models which need be considered to explain optical activity are those involving coupled oscillators. The model originally proposed by Drude[9] involved only one oscillating particle, and its rejection by Born and Kuhn[9] has done much to strengthen the common belief, that single oscillators are neither adequate nor important in providing a mechanism. In the following we propose to show that electric fields known to be present in molecules actually endow single dispersion electrons with optical activity of the magnitude observed. Consequently we feel that more is to be gained by attempting to discuss the actual application of (10) to molecular models. That is what is done in this paper.*

2. A Simple Model for Optical Activity

A characteristic feature of the modern theory of atomic and molecular spectra is the use of what may be called the Hartree approximation, in which each electron in the system moves in an average field due to the average action on it of all the other atoms and the nuclei. The detailed coupling of the electrons may then be taken into account in higher approximations. It seems, therefore, that the best approach to optical activity is gained by studying some simple potential field, in which a single electron moves, of such a character as to give activity. Such a calculation will be made in this section and later sections will be devoted to the correlation of the simple model with the structure of actual molecules.

The force field, $V(x, y, z)$, must be such that it has no planes of symmetry and no center of symmetry. This is true because if there were such an element of symmetry then the states could be classified as even or odd with regard to this symmetry element, and $\mathbf{p}$ and $\mathbf{m}$ would have selection rules of opposite kind with regard to

[3] Born, Physik. Zeits. **16**, 251, 437 (1915); Ann. d. Physik **55**, 177 (1917).
[4] Oseen, Ann. d. Physik **48**, 1 (1915).
[5] Gray, Phys. Rev. **7**, 472 (1916).
[6] Kuhn, Zeits. f. physik. Chemie **B4**, 14 (1929); Trans. Faraday Soc. **26**, 293 (1930).
[7] Born, Proc. Roy. Soc. **A150**, 84 (1935).
[8] Oke, Proc. Roy. Soc. **A153**, 339 (1935).
[9] See: Lowry, *Optical Rotatory Power*, p. 372 f. Kuhn has actually demonstrated that Drude's result was obtained by unjustifiably neglecting certain terms.

* *Added in proof:* These remarks, of course, do not apply to the recent important paper of Kirkwood, J. Chem. Phys. **5**, 479 (1937) who has taken steps toward the use of (10) in definite molecular models.

this character so there would be no states a and b for which $(a|\mathbf{p}|b)$ and $(b|\mathbf{m}|a)$ were both different from zero.

A simple field satisfying this requirement is given by

$$V(x_1x_2x_3)=(1/2)(k_1x_1^2+k_2x_2^2+k_3x_3^2)+Ax_1x_2x_3, \quad (14)$$

where the Cartesian coordinates of the particle are x_1, x_2, x_3. The motion of a particle of mass μ in such a field may be treated by the standard form of perturbation theory, treating the $Ax_1x_2x_3$ term as a perturbation.

In the zeroth approximation the energy levels are given by

$$W(n_1, n_2, n_3)=(n_1+\tfrac{1}{2})h\nu_1+(n_2+\tfrac{1}{2})h\nu_2+(n_3+\tfrac{1}{2})h\nu_3 \quad (15)$$

and the zero-order wave functions are

$$\psi(n_1, n_2, n_3)=\varphi_{n_1}(x_1/a_1)\varphi_{n_2}(x_2/a_2)\varphi_{n_3}(x_3/a_3), \quad (16)$$

in which

$$2\pi\nu_i=(k_i/\mu)^{\frac{1}{2}}, \quad (2\pi a_i)^2=h/\mu\nu_i; \quad (17)$$

and the φ functions are the normalized orthogonal system involving the Hermitian polynomials

$$\varphi_n(\xi)=(2^n n!\,\pi^{\frac{1}{2}})^{-\frac{1}{2}}H_n(\xi)e^{-\xi^2/2}. \quad (18)$$

The calculation of the matrix components of the perturbation energy $Ax_1x_2x_3$ with respect to the wave functions (16) is very readily made since the perturbation energy and the wave functions each factor into simple functions of an individual coordinate. Since the recursion formula for the functions (18) can be written

$$\xi\varphi_n(\xi)=[(n+1)/2]^{\frac{1}{2}}\varphi_{n+1}(\xi)+(n/2)^{\frac{1}{2}}\varphi_{n-1}(\xi), \quad (19)$$

the nonvanishing matrix components of ξ are in a one-dimensional scheme

$$(n|\xi|n')=[(n)/2]^{\frac{1}{2}} \quad \text{where} \quad n'=n\pm1 \quad (20)$$

and (n) means the larger of n or n'. Hence the nonvanishing matrix components of the perturbation energy are given by

$$(n_1n_2n_3|Ax_1x_2x_3|n_1'n_2'n_3')=Aa_1a_2a_3\,8^{-\frac{1}{2}}[(n_1)(n_2)(n_3)]^{\frac{1}{2}} \quad (21)$$

where $n_1'=n_1\pm1$, $n_2'=n_2\pm1$ and $n_3'=n_3\pm1$ and (n_i) means the larger of n_i and n_i'. It will be convenient to introduce an abbreviation

$$\lambda=Aa_1a_2a_3/8^{\frac{1}{2}}h. \quad (22)$$

Then by the standard perturbation theory we see that to the first order the energy levels remain the same as (15) since the diagonal elements of the perturbation vanish. The first-order perturbed wave function is

$$\Psi(n_1n_2n_3)=\psi(n_1n_2n_3)-\sum_{n_i'}\frac{\psi(n_1'n_2'n_3')(n_1'n_2'n_3'|Ax_1x_2x_3|n_1n_2n_3)}{W(n_1'n_2'n_3')-W(n_1n_2n_3)}, \quad (23)$$

where the summation contains at most eight terms because of the simplicity of (21).

Now for the optical activity one needs the matrix components of $\mathbf{r}$ and $\mathbf{L}$, the orbital angular momentum calculated with respect to the perturbed wave functions (23). Denoting these with square brackets and matrix components with respect to unperturbed functions with round brackets one has, to the first approximation for any quantity F,

$$[n_1n_2n_3|F|n_1'n_2'n_3']=(n_1n_2n_3|F|n_1'n_2'n_3')-\lambda\{\bar{\psi}_1(n_1n_2n_3)F\psi(n_1'n_2'n_3')+\bar{\psi}(n_1n_2n_3)F\psi_1(n_1'n_2'n_3')\}, \quad (24)$$

in which $\lambda\psi_1(n_1n_2n_3)$ is written for the second term on the right side of (23) and where $\bar{\psi}_1F\psi$ means that the expression is to be integrated over the configuration space.

The matrix components of $\mathbf{r}$ with regard to the unperturbed functions follow at once from (20) the result being

$$(n_1n_2n_3|\mathbf{r}|n_1'n_2'n_3')=2^{-\frac{1}{2}}\{\mathbf{i}(n_1)^{\frac{1}{2}}\delta(n_2, n_2')\delta(n_3, n_3')a_1+\mathbf{j}(n_2)^{\frac{1}{2}}\delta(n_1, n_1')\delta(n_3, n_3')a_2+\mathbf{k}(n_3)^{\frac{1}{2}}\delta(n_1, n_1')\delta(n_2, n_2')a_3\}. \quad (25)$$

Here $\mathbf{i}$, $\mathbf{j}$ and $\mathbf{k}$ are the usual unit vectors and $\delta(x, y)=0$ for $y\neq x$ and 1 for $y=x$. Hence to get nonvanishing matrix components two of the n's must be unchanged and the third must be given by $n_i'=n_i\pm1$.

The matrix components of **L** with regard to the unperturbed functions may be obtained as follows: from the theory of the Hermite polynomials in one dimension one has for the momentum operator p,

$$p\varphi_n=\frac{ih}{a}[\tfrac{1}{2}(n+1)]^{\frac{1}{2}}\varphi_{n+1}-\frac{ih}{a}[\tfrac{1}{2}n]^{\frac{1}{2}}\varphi_{n-1}. \tag{26}$$

From the definition of orbital angular momentum **L**,

$$L_1=x_2p_3-x_3p_2,$$

so using (19) and (26)

$$L_1\psi(n_1n_2n_3)=\frac{iha_2a_3}{2}\sum[\pm a_3^{-2}\mp a_2^{-2}][(n_2)(n_3)]^{\frac{1}{2}}\psi(n_1, n_2\pm1, n_3\pm1), \tag{27}$$

in which the $\sum$ extends over the four possible signs for $n_2\pm1$ and $n_3\pm1$ taken independently and where the sign choice on $\pm a_i^2$ is the same as that on $n_i\pm1$. As before (n_2) means the larger of n_2 or $n_2\pm1$. The expressions for $L_2\psi(n_1n_2n_3)$ and $L_3\psi(n_1n_2n_3)$ may be written down by cyclic permutation of the indices 1, 2, 3. In other words the nonvanishing unperturbed matrix components of **L** are therefore

$$\begin{aligned}
(n_1, n_2\pm1, n_3\pm1\,|\,L_1\,|\,n_1n_2n_3)&=\frac{iha_2a_3}{2}\left(\pm\frac{1}{a_3^2}-\pm\frac{1}{a_2^2}\right)[(n_2)(n_3)]^{\frac{1}{2}},\\
(n_1\pm1, n_2, n_3\pm1\,|\,L_2\,|\,n_1n_2n_3)&=\frac{iha_3a_1}{2}\left(\pm\frac{1}{a_1^2}-\pm\frac{1}{a_3^2}\right)[(n_3)(n_1)]^{\frac{1}{2}},\\
(n_1\pm1, n_2\pm1, n_3\,|\,L_3\,|\,n_1n_2n_3)&=\frac{iha_1a_2}{2}\left(\pm\frac{1}{a_1^2}-\pm\frac{1}{a_1^2}\right)[(n_1)(n_2)]^{\frac{1}{2}}.
\end{aligned} \tag{28}$$

From (28) and (25) it is obvious why an ordinary anisotropic harmonic oscillator is not optically active, for the nonvanishing matrix components in (25) require that two n's be unchanged whereas in (28) only one n is unchanged; hence there are no pairs of levels $(n_1n_2n_3)$ and $(n_1'n_2'n_3')$ for which both the **r** and the **L** matrix components have a nonvanishing value.

The optical activity is produced by the perturbing effect of the $Ax_1x_2x_3$ term by means of the terms proportional to λ in (24). For the sake of clarity and in view of the applications to be made, it will be sufficient to work out in detail the special case of activity due to molecules in the lowest state (000). Consideration of (23) combined with (21) shows that the perturbed wave function for (000) involves only (000) and (111) wave functions,

$$\Psi(000)=\psi(000)-\frac{\lambda}{\nu_1+\nu_2+\nu_3}\psi(111).$$

Hence by (25) the only states for which $[000\,|\,\mathbf{r}\,|\,n_1n_2n_3]$ has a nonvanishing zero-order value are (100), (010) and (001). These are the ordinary one-quantum jumps of the anisotropic oscillator. For these transitions **L** has a vanishing zero-order matrix component but a nonvanishing first-order component owing to the fact that by (23) and (21), $\Psi(100)$ contains $\psi(001)$. More explicitly

$$\Psi(100)=\psi(100)-\frac{\lambda 2^{\frac{1}{2}}}{\nu_1+\nu_2+\nu_3}\psi(211)+\frac{\lambda}{-\nu_1+\nu_2+\nu_3}\psi(011)$$

so using (24) and (28)

$$[100|\mathbf{L}|000]=-\frac{i\lambda h(a_2^2-a_3^2)}{2a_2a_3}\left[\frac{2\nu_1}{(\nu_2+\nu_3)^2-\nu_1^2}\right]\mathbf{i}, \tag{29}$$

and by cyclic substitution the formulas for $[010|\mathbf{L}|000]$ and $[001|\mathbf{L}|000]$ can be written down. Hence the three absorption lines (000→100) (000→010) and (000→001) give rise to optical activity in the first order, the appropriate strengths as occurring in (10) being given by

$$[000|\mathbf{r}|100]\cdot[100|\mathbf{L}|000]=-i\frac{Ah^2}{128\pi^5\mu^2}\left(\frac{1}{\nu_2}-\frac{1}{\nu_3}\right)\frac{1}{(\nu_2+\nu_3)^2-\nu_1^2}; \tag{30}$$

the other two of similar type being obtainable by cyclic substitution. As the right-hand side of (30) is pure imaginary, the imaginary part needed for (10) is just equal to the right-hand side of (30) with the i omitted.

These three lines therefore give rise to optical activity of the first order in virtue of zero-order matrix components of $\mathbf{r}$ combined with the first-order contributions to the matrix components of $\mathbf{L}$. Similarly there are three more lines which will give first-order optical activity in virtue of the first-order change in the matrix components of $\mathbf{r}$ combined with the zero-order matrix components of $\mathbf{L}$. These two sets of lines will exhaust the possibilities for optical activity of the ground state to the first order in the asymmetry coefficient A.

There will be an interesting contrast in type of the two sets of lines. For the set given by (30) the ordinary optical absorption will be strong since $[a|\mathbf{r}|b]$ has a nonvanishing zero-order value. But for the other type, whose optical activity is of the same order of magnitude, the ordinary optical absorption will be weak. Thus the model gives a division of the critical frequencies into two types —both of comparable contribution to the rotatory power but one strong in absorption, the other weak. This corresponds to a general experimental fact as recognized by Kuhn and interpreted by him in terms of the crossed oscillator model.

The states for which $[n_1n_2n_3|\mathbf{L}|000]$ has a nonvanishing zero-order value are, by (28), (110), (101) and (011). For these we need to calculate the first-order matrix components of $\mathbf{r}$ by a combination of (24), (23) and (25). The result is

$$[000|\mathbf{r}|011]=2^{\frac{1}{2}}\lambda a_1\frac{\nu_1}{(\nu_2+\nu_3)^2-\nu_1^2}\mathbf{i}, \tag{31}$$

the other two being obtained by cyclic substitution. Hence for this line the contribution to the optical activity is given by

$$[000|\mathbf{r}|011]\cdot[011|\mathbf{L}|000]=+i\frac{Ah^2}{128\pi^5\mu^2}\left(\frac{1}{\nu_2}-\frac{1}{\nu_3}\right)\frac{1}{(\nu_2+\nu_3)^2-\nu_1^2}, \tag{32}$$

the other two being obtained by cyclic substitution. It is interesting to note that (32) is exactly equal and opposite to (30). Hence the sum of the rotatory strengths associated with the jumps (000)→(100) and (000)→(011) is zero, verifying the general sum rule for the numerators in the rotatory dispersion formula.

The general sum rule is that the sum of the numerators in (10) is zero. This may be proved very simply. One has for this sum

$$\mathrm{Im}\{\sum_b(a|\mathbf{p}|b)\cdot(b|\mathbf{m}|a)\}=\mathrm{Im}\{(a|\mathbf{p}\cdot\mathbf{m}|a)\}$$

by the matrix law of multiplication. The quantity on the right vanishes since $(a|\mathbf{p}\cdot\mathbf{m}|a)$ is a diagonal matrix element of a real observable and hence is real.

In view of the fact that $\mathbf{p}=e\mathbf{r}$ and $\mathbf{m}=(e/2\mu c)\mathbf{L}$ for a single charged particle one can write down

the complete formula for the parameter β by combining (10), (30) and (32). The result is

$$\beta_{000}=\frac{Ahe^2}{12(2\pi)^5\mu^3}\left\{\left(\frac{1}{\nu_2}-\frac{1}{\nu_3}\right)\frac{1}{(\nu_2+\nu_3)^2-\nu_1^2}\left[-\frac{1}{\nu_1^2-\nu^2}+\frac{1}{(\nu_2+\nu_3)^2-\nu^2}\right]+\left(\frac{1}{\nu_3}-\frac{1}{\nu_1}\right)\frac{1}{(\nu_3+\nu_1)^2-\nu_2^2}\right.$$
$$\left.\times\left[-\frac{1}{\nu_2^2-\nu^2}+\frac{1}{(\nu_3+\nu_1)^2-\nu^2}\right]+\left(\frac{1}{\nu_1}-\frac{1}{\nu_2}\right)\frac{1}{(\nu_1+\nu_2)^2-\nu_3^2}\left[-\frac{1}{\nu_3^2-\nu^2}+\frac{1}{(\nu_1+\nu_2)^2-\nu^2}\right]\right\}. \quad (33)$$

It will be noticed that if any two of the frequencies ν_1, ν_2, ν_3 are equal the whole expression vanishes. This is in accord with the symmetry properties, for if, say, ν_2 and ν_3 are equal this implies k_2 and k_3 are equal so the harmonic oscillator potential has the x_1 axis as an axis of symmetry and therefore any plane through this axis is a plane of symmetry for the harmonic oscillator potential. Now $x_1x_2x_3$ has the plane $x_2=x_3$ as a plane of symmetry so if $\nu_2=\nu_3$ the plane $x_2=x_3$ is a plane of symmetry of the model so the optical activity should vanish.

By combining (33) with (7) or (8) one has an explicit formula for the rotatory power of a molecule which contains electrons moving in a field of the type postulated in (14).

3. Optical Activity of the Model in Higher Quantum States. Classical Mechanics as a Limiting Case

The extension of the preceding calculation to states with three arbitrary quantum numbers $(n_1n_2n_3)$ instead of (000) is of considerable interest not only because it applies to media with part of their molecules in excited states but also because the generalized formula taking the place of (33) leads for high quantum numbers asymptotically, in the sense of the correspondence principle, to an expression for the rotatory power of the classical model. We shall see that in going to this limit the system retains a finite rotatory power, and a simple expression in terms of the amplitudes will be given.

The procedure is of course closely analogous to the derivation previously given for the ground state. Again we start from Eqs. (10), (23), (25) and (28). When applied to our model, Eq. (23) gives:

$$\Psi(n_1n_2n_3)=\psi(n_1n_2n_3)-\lambda\sum\psi(n_1\pm1,\ n_2\pm1,\ n_3\pm1)\frac{[(n_1)(n_2)(n_3)]^{\frac{1}{2}}}{\pm\nu_1\pm\nu_2\pm\nu_3}, \quad (34)$$

where the summation is over all possible sign combinations and where equal signs are taken for the change of quantum number in any of the three axes, n_i, and the corresponding ν_i in the denominator. Consequently one obtains

$$[n_1n_2n_3|\mathbf{r}|n_1'n_2'n_3']\cdot[n_1'n_2'n_3'|L|n_1n_2n_3]=$$
$$-\lambda\sum\frac{[(n_1)(n_2)(n_3)]^{\frac{1}{2}}}{\pm\nu_1\pm\nu_2\pm\nu_3}\{(n_1n_2n_3|\mathbf{r}|n_1'n_2'n_3')(n_1'n_2'n_3'|\mathbf{L}|n_1\pm1\ n_2\pm1\ n_3\pm1)$$
$$+(n_1\pm1\ n_2\pm1\ n_3\pm1|\mathbf{r}|n_1'n_2'n_3')(n_1'n_2'n_3'|\mathbf{L}|n_1n_2n_3)\}+$$
$$-\lambda\sum\frac{[(n_1')(n_2')(n_3')]^{\frac{1}{2}}}{\pm\nu_1\pm\nu_2\pm\nu_3}\{(n_1n_2n_3|\mathbf{r}|n_1'n_2'n_3')(n_1'\pm1\ n_2'\pm1\ n_3'\pm1|\mathbf{L}|n_1n_2n_3)$$
$$+(n_1n_2n_3|\mathbf{r}|n_1'\pm1\ n_2'\pm1\ n_3'\pm1)(n_1'n_2'n_3'|\mathbf{L}|n_1n_2n_3)\}. \quad (35)$$

The zero-order term $(n|\mathbf{r}|n')\cdot(n'|\mathbf{L}|n)$ is absent in (35) because the selection rules of $\mathbf{r}$ and $\mathbf{L}$ mutually exclude each other in the unperturbed case which has three planes of symmetry. The following transitions are found to contribute to $(n|x|n')(n'|L_x|n)$:

(a)	$(n_1n_2n_3)\rightarrow(n_1+1,\ n_2,\ n_3)$,	(d)	$\rightarrow(n_1,\ n_2-1,\ n_3+1)$,
(b)	$\rightarrow(n_1-1,\ n_2,\ n_3)$,	(e)	$\rightarrow(n_1,\ n_2+1,\ n_3-1)$,
(c)	$\rightarrow(n_1,\ n_2+1,\ n_3+1)$,	(f)	$\rightarrow(n_1,\ n_2-1,\ n_3-1)$.

If we denote these six transitions for brevity by letters a to f in the order listed, it is easily seen that a and b, c and f, d and e have equal and opposite transition frequencies, namely $\pm\nu_1$, $\pm(\nu_2+\nu_3)$ and $\pm(\nu_2-\nu_3)$ respectively. Since transition frequencies $\nu_{nn'}$ enter into (10) for β, in the second power, each pair of transitions will jointly give rise to one dispersion term of the general type that was previously obtained in Eq. (30). Actually it is found that only the first and third term in (35) will contribute by virtue of a transition a or b, and similarly only the second and the fourth term of (35) contribute in transitions c, d, e, f. There are, in all, 32 terms to be considered for the matrix product $(n|x|n')(n'|L|n)$ and 64 more terms are obtained by cyclic substitution to give contributions toward the y and the z matrix components. A simple though lengthy calculation leads after much simplification and canceling to the final formula for β:

$$\begin{aligned}\beta_{n_1n_2n_3}=\frac{Ahe^2}{12(2\pi)^5\mu^3}\Bigg\{&\left(\frac{1}{\nu_2}-\frac{1}{\nu_3}\right)\frac{(n_2+n_3+1)}{(\nu_2+\nu_3)^2-\nu_1^2}\left[-\frac{1}{\nu_1^2-\nu^2}+\frac{1}{(\nu_2+\nu_3)^2-\nu^2}\right]\\&+\left(\frac{1}{\nu_2}+\frac{1}{\nu_3}\right)\frac{(n_2-n_3)}{(\nu_2-\nu_3)^2-\nu_1^2}\left[-\frac{1}{\nu_1^2-\nu^2}+\frac{1}{(\nu_2-\nu_3)^2-\nu^2}\right]\\&+\left(\frac{1}{\nu_3}-\frac{1}{\nu_1}\right)\frac{(n_3+n_1+1)}{(\nu_3+\nu_1)^2-\nu_2^2}\left[-\frac{1}{\nu_2^2-\nu^2}+\frac{1}{(\nu_3+\nu_1)^2-\nu^2}\right]\\&+\left(\frac{1}{\nu_3}+\frac{1}{\nu_1}\right)\frac{(n_3-n_1)}{(\nu_3-\nu_1)^2-\nu_2^2}\left[-\frac{1}{\nu_2^2-\nu^2}+\frac{1}{(\nu_3-\nu_1)^2-\nu^2}\right]\\&+\left(\frac{1}{\nu_1}-\frac{1}{\nu_2}\right)\frac{(n_1+n_2+1)}{(\nu_1+\nu_2)^2-\nu_3^2}\left[-\frac{1}{\nu_3^2-\nu^2}+\frac{1}{(\nu_1+\nu_2)^2-\nu^2}\right]\\&+\left(\frac{1}{\nu_1}+\frac{1}{\nu_2}\right)\frac{(n_1-n_2)}{(\nu_1-\nu_2)^2-\nu_3^2}\left[-\frac{1}{\nu_3^2-\nu^2}+\frac{1}{(\nu_1-\nu_2)^2-\nu^2}\right]\Bigg\}.\end{aligned}\tag{36}$$

This clearly contains the previous result, (33), as a special case, but also exhibits some new features. First of all we have now three resonance frequencies for the rotatory dispersion, instead of the two previously obtained. Of these, ν_1, represents a frequency which is also strongly pronounced in absorption, but there are now two weak absorption bands $(\nu_2+\nu_3)$ and $(\nu_2-\nu_3)$ which may exhibit strong rotatory power. Again the sum rule is obviously fulfilled as the numerator going with the strong absorption frequency is equal and opposite to the sum of the other two. Eq. (36) may also be written in a slightly modified form:

$$\begin{aligned}\beta_{n_1n_2n_3}=-\frac{Ahe^2}{12(2\pi)^5\mu^3}\sum_{\text{cycl.}}\Bigg\{&\left(\frac{1}{\nu_k}-\frac{1}{\nu_l}\right)\frac{(n_k+n_l+1)}{[(\nu_k+\nu_l)^2-\nu^2][\nu_i^2-\nu^2]}\\&+\left(\frac{1}{\nu_k}+\frac{1}{\nu_l}\right)\frac{(n_k-n_l)}{[(\nu_k-\nu_l)^2-\nu^2][\nu_i^2-\nu^2]}\Bigg\}.\end{aligned}\tag{36a}$$

Here $\sum_{\text{cycl.}}$ means sum over $(kli)=(2,3,1)$, $(3,1,2)$ and $(1,2,3)$.

In order to derive a limiting expression for β in terms of the amplitudes $A_1A_2A_3$ of the particle's motion in the three axial directions we express the quantum numbers in terms of the amplitudes by means of the energy relation valid for a harmonic oscillator:

$$\begin{aligned}n_1h\nu_1&=(1/2)k_1A_1^2=2\pi^2\nu_1^2A_1^2\mu,\\h\nu_1&=2\pi^2\mu A_1\nu_1^2,\end{aligned}\tag{37}$$

and two similar equations for the other two quantum numbers. Substituting from (37) into (36) we have at once

$$\beta(A_1A_2A_3)=\frac{e^2A}{384\pi^4\mu^2}\Bigg\{\left(\frac{1}{\nu_2}-\frac{1}{\nu_3}\right)\frac{\nu_2A_2^2+\nu_3A_3^2}{(\nu_2+\nu_3)^2-\nu_1^2}\left[-\frac{1}{\nu_1^2-\nu^2}+\frac{1}{(\nu_2+\nu_3)^2-\nu^2}\right]$$
$$+\left(\frac{1}{\nu_2}+\frac{1}{\nu_3}\right)\frac{\nu_2A_2^2-\nu_3A_3^2}{(\nu_2-\nu_3)^2-\nu_1^2}\left[-\frac{1}{\nu_1^2-\nu^2}+\frac{1}{(\nu_2-\nu_3)^2-\nu^2}\right]$$
$$+\text{four more lines obtained from these by cyclic permutation of the indices}\Bigg\}. \quad (38)$$

This result does not contain h or other quantum-mechanical concepts and represents in the limit, according to the correspondence principle, the response of our model if it were a system obeying classical mechanics.

4. Qualitative Properties of the Field

Before discussing the application of the results of Section 2 to actual molecules it is worth while to form a mental picture of the kind of potential field represented by (14). This is best done by considering the shape of the equipotential surfaces. Suppose for definiteness that $k_1>k_2>k_3$ and at first that $A=0$. Then the equipotential surfaces will be ellipsoids whose principal axes are the coordinate axes and whose axes increase in the order $x_1<x_2<x_3$. The sections of any such ellipsoid by a plane $x_3=$constant will then be ellipses all of whose principal axes are parallel to the x_1 and x_2 axes. Now suppose that the $Ax_1x_2x_3$ term is present, say with $A>0$. Then the equation of the intersection of an equipotential with the plane $x_3=Z$ is

$$\frac{k_1}{2}x_1^2+\frac{k_2}{2}x_2^2+AZx_1x_2=(V-\tfrac{1}{2}k_3Z^2).$$

This is the equation of an ellipse whose axes have been twisted relative to parallelism with the x_1 and x_2 axes in the counter-clockwise sense as viewed from the positive x_3 axis, the angle of twist being θ where

$$\tan 2\theta=\frac{AZ}{\tfrac{1}{2}(k_1-k_2)}. \quad (39)$$

The angle of twist therefore increases with increasing Z, in other words the equipotential surface is a kind of twisted ellipsoid something like what one might get if an ordinary ellipsoid of three unequal axes were subjected to a tortional stress twisting it around the x_3 axis in the sense of a right-handed screw. The angle through which an axis is twisted can never exceed 45°.

Similarly the sections of the equipotentials by the planes $x_1=X$ are also ellipses which are skewed around in the same screw sense for the angle of twist is given by (39) with the cyclic substitutions $Z\to X$, $k_1\to k_2$, $k_2\to k_3$ and the sense remains the same because we have assumed $k_2>k_3$. The sections of the equipotentials by the planes $x_2=Y$ are also a set of ellipses, but they are skewed around in the opposite sense for the form of (39) applicable to this case involves (k_3-k_1) in the denominator which is negative in the case we are discussing.

It should be clear that no matter what are the relative magnitudes of k_1, k_2 and k_3 the situation will always be the same in that the sections of the equipotential surface by planes parallel to any of the coordinate planes will be sets of ellipses, two of which screw around in the same sense while the third has the opposite screw sense.

Comparing these qualitative properties of the field with the formula (33) for β_{000} we see that if $A>0$ and $k_1>k_2>k_3$ then the ν_1 and ν_3 absorption lines contribute positive quantities to β while the ν_2 line contributes a negative quantity. There is, therefore, an absolute correlation of the screw sense in the potential field and the sign of the contribution to β. The rule is: *the contribution to the rotation of the absorption line ν_i is dextro-rotatory if the screw sense of the equipotential surfaces with regard to the x_i axis is positive.* This rule affords a basis for discussion

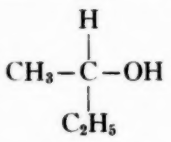
of the age-old problem of absolute configuration in optically active molecules.

The rule is exactly what one would expect from a simple consideration of the relation of the field to formula (4). The absorption line ν_3 corresponds to the excitation of a vibratory motion that is essentially parallel to the x_3 axis. Owing to the spread of the wave function in the x_1 and x_2 directions the motion is not confined entirely to motion precisely along the x_3 axis. Owing to the screw twist in the field there is a corresponding screw twist in the wave functions so the electron tends to screw around in a somewhat helical way, following the places where the potential energy is least. Suppose now the motion is in phase with the electric vector, then the velocity will be in phase with $\dot{E}$ and so owing to the particle's following a somewhat helical path there will be a circular current around the x_3 axis, in phase with which will produce the effective induced magnetic moment $\mathbf{m}_1$, directed along the x_3 axis and so vectorially proportional to the $\dot{E}$ which produced it.

The induction of an electric moment vectorially proportional to $\dot{H}$ but of opposite sign as in (4) may also be easily visualized. Suppose that $\dot{H}$ is parallel to the x_3 axis. Then it corresponds to a rate of change of flux through the x_1x_2 plane which therefore is accompanied by induced electromotive forces tending to make the electron move around in the x_1x_2 plane in the clockwise, or negative sense, owing to Lenz's law for induced currents. Owing to the helical constraints, when the electron does this it is caused to move toward the $-x_3$ direction and thus to produce an electric moment in the direction $-\dot{H}$ as given by (4). (The foregoing statements are made for a positive electron—for a negative electron the results are the same because change in sign not only reverses the direction of the forced motion but also reverses the sense of the moments resulting from the forced motion, corresponding to the occurrence of e^2 in (33).)

5. Adaptation of the Model to Actual Molecules

The simplest kind of optically active molecule conceivable is that in which four different single atoms are attached to a central carbon atom. Such compounds have never been prepared, at least not in active form. The next simplest type is that in which the four attachments to a central carbon atom may be organic radicals, as in the case of secondary butyl alcohol,



Such a molecule will be characterized by a very complicated electronic absorption spectrum, lying entirely in the ultraviolet in the case of colorless liquids. The absorption spectrum is complicated not only because of the large number of electronic transitions possible but also because of the complexity of structure arising from the great variety of vibrational and rotational jumps which can be associated with a given electronic jump. In the face of such a complex situation some simplifying assumptions must be made.

Study of polyatomic absorption in the ultraviolet has shown that it is possible in most cases to associate a given set of bands with an electron transition occurring in a fairly definite part of the molecule. The group of atoms or radical in which the transition occurs is then said to be the chromophoric group or the chromophore for that system of bands.

The optical activity associated with a given electronic jump in the molecule arises essentially from the cooperation of two factors: (1) the electronic jump occurs in the molecule in a fairly well-localized place in some definite group in the molecule, (2) the electron which makes a transition is moving in a force field principally due to the immediate atoms to which it belongs, but secondarily due to the fields set up by the effective charge distributions of the other atoms in the molecules. It is the contribution of the neighboring atoms to the force field in which the chromophoric electron moves which is responsible for the optical activity.

This action of neighboring groups on the chromophoric group has generally been called *vicinal action* in a general way. In what follows we give a more precise picture of the nature of vicinal action.

Of course any electron in the molecule is the

chromophoric electron for those transitions in which its state changes. But the important electron transitions will be those lying in the near ultraviolet which will mean that those electrons contained in groups that absorb in the near ultraviolet, or in the visible when present, will dominate the situation. This statement is much nearer the truth here than in the case of ordinary refraction for here the contributions to β of different bands in the deep ultraviolet are of different sign and so tend to cancel whereas in ordinary refraction they are all of the same sign so the cumulative effect of many of them may be considerable.

Suppose, for example, that the chromophoric electron in the near ultraviolet is a bonding electron between C and the OH in secondary butyl alcohol. Then in the absence of the other groups, of if the three other groups were all alike, the effective field in which that electron would move has the C−O direction as an axis of symmetry and would be more extended along the bond direction than transverse to it. The equipotential surfaces would be shaped like rather prolate ellipsoids of revolution. The actual space dependence of the potential energy would, of course, go asymptotically to a constant value like the Coulomb law for large distances.

Now the behavior of the field at large distances does not matter much if we confine ourselves to the two lowest states for in these the wave functions are essentially confined to a small region near the potential minimum. Therefore for discussion of the two lowest states it will be fairly accurate to represent the effective field due to the C and O atoms by a harmonic oscillator potential, having the C−O line as an axis of revolution. Choosing the C−O direction as the Z axis the potential will then be approximately

$$V_0=\tfrac{1}{2}k_1(x_1^2+x_2^2)+\tfrac{1}{2}k_3z^2, \qquad (40)$$

where the origin of coordinates will be somewhere between the carbon and oxygen nuclei at a place that can only be made definite on the basis of more exact information about the actual molecular orbitals in this bond.

Next we have to consider the way in which (40) is affected by the vicinal action of the neighboring groups. As a preliminary, consider the potential

$$U=[(X_1-x_1)^2+(X_2-x_2)^2+(X_3-x_3)^2]^{-\frac{1}{2}} \qquad (41)$$

at the position (x_1, x_2, x_3) due to unit charge located at $X_1X_2X_3$. If $x_1x_2x_3$ are all small compared to $X_1X_2X_3$ as will be the case if $x_1x_2x_3$ are the coordinates of the chromophoric electron and $X_1X_2X_3$ are those of the distant vicinal group, then the potential can be developed as

$$U=\frac{1}{R}-x_i\frac{\partial}{\partial X_i}\left(\frac{1}{R}\right)+\tfrac{1}{2}x_ix_j\frac{\partial^2}{\partial X_i\partial X_j}\left(\frac{1}{R}\right)$$
$$-\frac{1}{6}x_ix_jx_k\frac{\partial^3}{\partial X_i\partial X_j\partial X_k}\left(\frac{1}{R}\right), \qquad (42)$$

in which summations over repeated indices are implied and $R=[X_1^2+X_2^2+X_3^2]^{\frac{1}{2}}$. The constant term is of no interest, since the zero of energy has to be arbitrarily fixed anyway. The linear terms represent a certain general average field acting on the electron which will produce a slight displacement of the equilibrium position.

The important terms in (41) for application of the results of Section 2 are the quadratic and the cubic. The total action of the charge distribution in the vicinal groups will be obtained by summing (37) over the charges in the vicinal groups. The quadratic and cubic terms coming from the summed expression may be written

$$\tfrac{1}{2}a_{ij}x_ix_j+\tfrac{1}{6}b_{ijk}x_ix_jx_k. \qquad (43)$$

These have to be added to (40) to get our approximation to the full field in which the chromophoric electron moves. The terms in (43) are supposed to be small compared with those in (41).

Considering first the effect of adding the quadratic part of (43) to (40) we see that the resulting harmonic potential will in general be one in which the principal axes are tilted with respect to the original coordinate axes and in which the axis of symmetry has, in general, been removed. The tilting of one principal axis (x_3) away from the bond axis will in general be negligibly small if the original field V_0 is sufficiently anisotropic, i.e., if the cross terms a_{13} and a_{23} (which cause the tilting) are small compared with $|k_1-k_3|$ in (40). Neglecting this slight tilting amounts to neglecting completely the a_{13}, and a_{23} terms. The terms involving a_{11} a_{12} and a_{22} however are important for it is

these which determine the previously indeterminate principal axes by removing the symmetry of (40) about the x_3 axis.

After adding the important quadratic part of (40) the dependence of the potential on x_1x_2 becomes

$$\tfrac{1}{2}(k_1+a_{11})x_1^2+a_{12}x_1x_2+\tfrac{1}{2}(k_1+a_{22})x_2^2.$$

A rotation of the axes through an angle γ is described by

$$\begin{aligned} x_1&=x_1'\cos\gamma-x_2'\sin\gamma \\ x_2&=x_1'\sin\gamma+x_2'\cos\gamma \end{aligned} \tag{44}$$

and the potential energy in terms of the x_1' and x_2' is

$$\begin{aligned} &\tfrac{1}{2}(k_1+a_{11}\cos^2\gamma+2a_{12}\sin\gamma\cos\gamma \\ &\qquad +a_{22}\sin^2\gamma)x_1'^2, \\ &+\tfrac{1}{2}(k_1+a_{11}\sin^2\gamma-2a_{12}\sin\gamma\cos\gamma \\ &\qquad +a_{22}\cos^2\gamma)x_2'^2, \end{aligned} \tag{45}$$

provided that γ has been chosen to make the coefficient of $x_1'x_2'$ vanish. The value of γ which does this is given by

$$\tan 2\gamma=\frac{2a_{12}}{a_{11}-a_{22}}. \tag{46}$$

Hence the important effect of the quadratic terms due to the vicinal groups is the removal of the axis of symmetry of the effective field of the chromophoric electron.

If now one transforms the cubic terms of (43) to the coordinate system (x_1', x_2', x_3) defined by (44) and (46) then the particular term which involves the product of the coordinates $x_1'x_2'x_3$ is the important one and is the term to be identified with the $Ax_1x_2x_3$ term of Section 2.

At first sight it might seem that all of the cubic terms in the potential would contribute to the optical activity and it is true that they do in higher approximations. But in the first approximation of the perturbation theory as used in Section 2 the contribution due to each cubic term would be linear in the coefficient of that term so the first approximation cannot take account of the joint action of several such terms. On the other hand, of the various kinds of cubic terms $Ax_1x_2x_3$ is the only one which removes all the planes of symmetry possessed by the harmonic oscillator potential, and therefore it is the only one which produces optical activity in the first approximation. For instance the potential x_1^3 leaves the x_1x_2 and x_1x_3 planes as planes of symmetry. A combined action of $(x_1^3+x_2^3+x_3^3)$ in the cubic potential would remove all the symmetry planes in the field but its contribution to the rotatory power would not appear in the first approximation as it depends on the joint presence of three cubic terms.

To summarize: we suppose the effective field in which the chromophoric electron would have moved if the vicinal action were neglected to be given by (40). As this is simply a formal representation to produce wave functions of approximately the correct spatial extent, one has to pick k_1 and k_3 in this to correspond to the frequencies of the lowest electronic jumps for the electron, the k's being related to the ν's by (17).

In general the bonding electron in this approximation will be a Σ electron and the first excited state corresponding to motion along the figure axis will also be a Σ state for the electron so k_3 is the oscillator force constant which gives the frequency through (17) of the lowest $\Sigma\rightarrow\Sigma$ electronic transition. Similarly the excited states corresponding to excitation of transverse motion will be Π states so k_1 will be chosen to make ν_1 the frequency of the lowest $\Sigma\rightarrow\Pi$ electron transition in that chromophore.

The next step consists in analyzing the probable charge distribution of the vicinal groups. If one had exact knowledge of the molecular orbitals this would be given at once by the density of the orbitals of the rest of the molecule. In the absence of such knowledge one has to try to piece together the main essentials by use of the results of dipole moment studies. These assign measured dipole moments to various bonds in the molecule which may be represented by net charges on the two atoms at opposite ends of a bond chosen so the product of net charge by bond distances is equal to bond dipole moment. This will be discussed later in connection with a specific example.

Finally with a known charge distribution, say charges e_s located at points X_{1s}, X_{2s}, X_{3s} one has to calculate the quadratic terms in the potential energy due to the charges of the vicinal group as in (41) and (42). This will determine the way

in which the axis of symmetry of the chromophoric field is removed through (44) and (46). Finally with axes chosen along the principal axes of the quadratic part of the chromophoric field of all the cubic potential terms one has to calculate only $Ax_1x_2x_3$. In this way we see that k_1 and k_3 are principally determined by the local field to which the chromophore electron belongs, while k_1-k_2 and A are determined by the fields of the vicinal groups.

The discussion may be made more precise by writing the explicit formulas for the important quantities. Calculating the derivations in (42) one finds for the potential energy of an electron of charge e in the vicinal field of charges $e_1 \cdots e_s \cdots$

$$a_{11}=e\sum_s e_s(3X_{1s}^2-R_s^2)\frac{1}{R_s^3}, \tag{48}$$

$$a_{12}=e\sum_s e_s\frac{3X_{1s}X_{2s}}{R_s^5}, \tag{49}$$

and a corresponding formula for a_{22}, obtained by substituting 2 for 1 in (48). Then the transformation to principal axes is given by (45) and (46). Finally the coefficient of the cubic term in the potential energy $Ax_1'x_2'x_3$ is given by

$$A=+(5/2)e\sum_s e_s\frac{X_{1s}'X_{2s}'X_{3s}}{R_s^7}, \tag{50}$$

in which X_{1s}' and X_{2s}' are coordinates of vicinal charges referred to the principal axis coordinate system defined by (44) and (46).

6. Application to Methyl Phenyl Carbinol Nitrite

We next proceed to test our thesis that coulombic force action from vicinal groups is responsible for the term $Ax_1x_2x_3$ in the potential function (14). To do this we compute the rotatory power of the nitrite band and the phenyl band in methyl phenyl carbinol nitrite.[10] In molecules containing the nitrite group $-O-N=O$ the existence of an absorption band well removed from the neighborhood of other bands, and in the experimentally accessible region around 3650A, provides a convenient means for such a study because here one can identify with reasonable assurance what part of the rotatory power measured at any given wave-length is contributed by that particular band. The nitrite contribution appears surprisingly rich in structural detail, superimposed on the much stronger and slowly varying contribution from the phenyl band. The assignment to phenyl follows from a comparison with methyl cyclohexyl carbinol nitrite, and with methyl *n*-hexyl carbinol nitrite. In both of these cases where the phenyl has been replaced by other substituents we find that the contribution allegedly coming from the phenyl band is suppressed as one would expect from this assignment.

In what follows we adopt with minor modifications the general outline given in Section 5. In one essential point, however, we allow our conception of the nitrite band to differ from an assumption made in that section. We regard the chromophoric electron which is instrumental in the nitrite absorption at 3650A as being isotropically bound to its equilibrium position; isotropically, that is, except for the perturbation effect which the electric dipole field from the other three groups exert upon it. In view of the presence of big charges in the nitrite group itself this assumption can hardly be more than an approximation. At the same time it is dictated by the very uncertain way in which these charges are distributed with respect to the rest of the molecule. Since the distribution varies with the free rotation of the ONO group around the single C–O bond the actual orientation of the "unperturbed" polarization ellipsoid is extremely elusive. If, then, we simply consider the unperturbed problem as threefold degenerate it is quite clear that in the perturbed case the orientation of all three principal axes will be sensitive to the perturbing field, and not merely two as was assumed in the last section. The remark should be added that, since the rotatory power of our model is proportional to the three differences between ν_1, ν_2 and ν_3, one must expect the resulting β to be small of higher order in the case where the frequencies are different from each other merely as a consequence of the perturbing field than if they had been different in the unperturbed oscillator.

[10] Kuhn and Biller, Zeits. f. physik. Chemie **B29**, 1 (1935).

In Section 5 it was explained that the numerical problem is essentially a determination of the asymmetry coefficient A of (50), when the potential has been referred to three axes $x_1'x_2'x_3'$ in which the quadratic terms of V reduce to a sum of squares. An isotropic oscillator which will absorb at 3650A, the absorption wave-length of the nitrite band, has three equal force constants $k_1=k_2=k_3=24{,}000$, in absolute units. Thus, to second-order terms the potential can be represented by

$$U_2=\sum_{ik}a_{ik}x_ix_k=12{,}000(x_1^2+x_2^2+x_3^2)$$
$$+\sum x_ix_k\sum_s\frac{ee_s}{2R_s^5}(3X_{is}X_{ks}-\delta_{ik}R_s^2),$$

where δ_{ik} is 1 or 0 depending on whether i and k are equal or not. This follows from (38) and (49). The second term of the above equation can be obtained from a list of coordinates of the individual vicinal charges e_s if these charges are referred to a right-handed coordinate system with the supposed chromophoric electron at the origin. We have tentatively chosen this position to coincide with the oxygen nearest to the asymmetric carbon atom. A list of coordinates and charges is given in Table I. The vicinal charges have been located at the position of the atoms so as to be compatible with the known bond moments and interatomic distances. The dipole moments used were: +0.35 for the CH bonds, −0.85 for the C−O, +0.30 for O−N, −2.15 for N=O. The last two moments were determined so as to give a resultant dipole moment of −1.90 for the nitrite group. All moments are given in Debye units. Zero bond moment has been assumed for the phenyl group.

TABLE I.

ATOM:	H_0	H_1	H_2	H_3	C_1	C_2	O_1
CHARGE:	0.28	0.28	0.28	0.28	−0.28	−0.84	0.00
X_1	0.93	−0.93	0.93	0.00	0.00	0.00	0.00
X_2	− .53	1.67	1.67	2.16	0.00	0.00	0.00
X_3	−1.80	−2.54	−2.54	−1.03	−1.43	−1.92	0.00

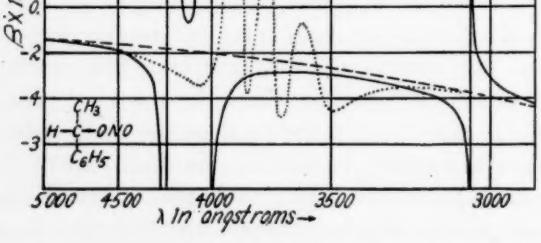


FIG. 1. Dotted curve, experimental $[M]$ values (Fig. 1a of Kuhn and Biller, Zeits. f. physik. Chemie **B29**, 1 (1935)) translated into B values. Broken line, estimated contribution of bands in far ultraviolet. Full lines, calculated.

Principal axes of U_2 as is well known are most conveniently determined by solving the homogeneous set of three linear equations

$$(a_{11}-k)u+a_{12}v+a_{13}w=0,$$
$$a_{21}u+(a_{22}-k)v+a_{23}w=0,$$
$$a_{31}u+a_{32}v+(a_{33}-k)w=0,$$

where k must be determined so that this set has a solution different from zero. In other words k must be a solution of the secular equation $|a_{ik}-\delta_{ik}k|=0$. For each of the three roots k_1', k_2', k_3' there exists one solution of the linear set which can be so normalized as to represent the direction cosines α_{i1}, α_{i2}, α_{i3} $(i=1, 2, 3)$, of the three principal axes. These α_{ik} represent the matrix of the linear orthogonal transformation which provides us with the coordinates X_1', X_2', X_3' of the vicinal charges in the new coordinate system. Using (50) one thus determines the numerical value of A for the nitrite absorption band in methyl phenyl carbinol nitrite to be

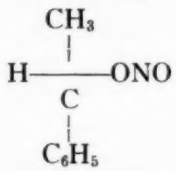
$$A=1.46\cdot10^{10}.$$

The new wave-lengths into which the threefold degenerate band at 3650 is split are the following: λ4215, λ4026 and λ3054. With the numerical values of A and ν_1, ν_2, ν_3 given one is in a position to apply (33) to calculate β as a function of the frequency of the incident light, and to compare it with the experimental dispersion curve as reported by Kuhn.[11] Fig. 1 gives the experimental values together with a theoretical curve which was obtained by adding the calculated contribution from the nitrite band to the part presumably coming from the phenyl band which can be fairly well estimated from the empirical curve by smooth interpolation (dotted curve). The

[11] W. Kuhn and H. Biller, Zeits. f. physik. Chemie **B29**, p. 1 (1935). See especially Fig. 1.

agreement between theory and experiment is satisfactory particularly in the long wave range of the diagram. As a matter of fact one should keep in mind that our oscillator model was primarily designed to represent the low energy quantum states approximately. But actual transitions which involve higher energies than $h\nu$ of the harmonic oscillator are probably not well represented by matrices derived from oscillator eigenfunctions, and the calculated energy differences are larger than the transition energies in the actual physical system.

An interesting consequence of the computation just given is that it implies an *absolute configuration* for the compound discussed. The absolute configuration for the methyl phenyl carbinol nitrite which we used in the above computation of A is



Our computation shows that this should be identified with the laevorotatory isomer. When chemists relate this compound to other *d*- or *l*-compounds their absolute configuration will automatically follow.

If one tries to compute the phenyl contribution using the assumption that the phenyl chromophor is bound isotropically to its equilibrium position, with force constants giving the absorption band of phenyl at 2600A, one obtains a value $A=0.83\cdot 10^{10}$, that is considerably smaller than was obtained for the contribution of the nitrite band. This calculation takes into account the perturbing effect of all the other three charges, including the nitrite group as the latter no doubt is the controlling factor in the production of an asymmetric field at the center of the phenyl group. The configuration most likely to occur on statistical grounds, and at the same time the one most effective in producing the desired effect is that configuration in which the nitrite group lies in the plane through the two bonds C_1-O and C_1-phenyl with the double-bonded oxygen in a position closest to the center of the phenyl group. In view of the large dipole moments of the nitrite group and the high polarizability of the phenyl group this configuration (or a very similar one) must be quite stable compared with others. The result of the calculation is instructive in the following detail. It is found that only about two percent of the total value calculated for A is caused by the highly charged oxygen nearest to the phenyl; the reason being that its charge determines the principal axes of the perturbed polarization ellipsoid to such an extent that, lying almost exactly in one of the new coordinate planes it contributes practically nothing to the sum $\Sigma e e_s R_s^{-7} X_{1s}' X_{2s}' X_{3s}$. On the other hand, our assumption that the phenyl chromophor is isotropically bound is far more objectionable according to all that is known about the electronic structure of the benzene ring, than was the analogous assumption in the case of the nitrite chromophor. As the phenyl electron is actually much more stiffly bound in the direction at right angles to the ring than in the other two directions, it will offer a certain amount of resistance to tilting of its principal axes, with the result that the oxygen will lie well away from all three coordinate planes and thus will contribute generously to the asymmetry factor A. In this connection it is interesting to see in a simple way how much a given charge e_s at a given distance R_s can at best contribute to A. Since the optimal position for e_s is to make equal angles with all three principal axes of U_2, it is easily seen from (50) that with

$$X_1'=X_2'=X_3'=R/(3)^{\frac{1}{2}},$$

$$A_{\max}=(5/2)\frac{ee_s}{R^4(27)^{\frac{1}{2}}}=\frac{229.5e_s}{R^4}10^{10},$$

e_s in 10^{-10} e.s.u., R in A.

Since the double-bonded nitrite oxygen represents a charge of $-1.76\cdot 10^{-10}$ e.s.u. at a distance $R=2.05$A, we find that its contribution to A might under favorable circumstances reach a value as big as 23×10^{10}. Rapidly diminishing optimal contributions are obtained for the other charges as their distance from the phenyl grows bigger ($A_{\max}=4.9\times 10^{10}$ for N, and $=1.13\cdot 10^{10}$ for O_1). On the whole one sees from this over-all estimate that a potential reservoir of rotatory power is available in our model of this compound which is easily sufficient to account for the observed big rotations associated with the phenyl group.

7. Quantum Mechanics of Circular Dichroism

Closely associated with optical activity is the phenomenon of circular dichroism which is observed experimentally as the Cotton effect.[12] The quantum-mechanical formulation of this effect is a fairly obvious extension of the ordinary theory of absorption transition probabilities but, as it appears not to have been worked out explicitly before, it is perhaps useful to work it out here.

The effect in question is that the absorption coefficients for right and left circularly polarized waves are different for the absorption bands which contribute to the optical activity. It may be worked out either by the original theory[13] in which the fields of the light wave are regarded as causing transitions, or by the quantized field method due to Dirac.[14] We shall use the former method as this involves somewhat simpler equations. The end result is the same by both methods, of course.

Suppose then the light wave is represented by a vector potential

$$\mathbf{A}=\tfrac{1}{2}[\mathbf{A}\exp[iE(t-\mathbf{k}\cdot\mathbf{r}/c)/\hbar] +\bar{A}\exp[-iE(t-\mathbf{k}\cdot\mathbf{r}/c)/\hbar]], \quad (51)$$

in which $E=h\nu$ and ν is the frequency of the light. The interaction energy of the light wave and the charges in the molecule is represented by

$$H=-(e/mc)\sum_i \mathbf{A}_i\cdot\mathbf{p}_i-(e/mc)\sum_i \mathbf{S}_i\cdot(\text{curl }\mathbf{A})_i, \quad (52)$$

the sum being over the various electrons in the molecule. The second term represents the direct interaction of the spin magnetic moment with the magnetic vecor of the light wave.

Let the molecule be initially in quantum state a and the light wave begin to act at $t=0$. Then for $t>0$ we can write

$$\Psi=\psi(a)\exp[-iW_at/\hbar]+\psi_1(a) \quad (53)$$

and the dynamical equation of quantum mechanics for $\psi_1(a)$ is

$$\left(H_0-i\hbar\frac{\partial}{\partial t}\right)\psi_1(a)=-H\psi(a)\exp(-iW_at/\hbar), \quad (54)$$

where H_0 is the Hamiltonian of the unperturbed molecule. This has to be solved with the initial condition, $\psi_1(a)=0$ for $t=0$. The solution is found in the usual way. Expand the right side of (54) in a series of unperturbed wave functions.

$$-H\psi(a)\exp(-iW_at/\hbar)=(1/2)\sum_b\psi(b) \times\exp(-iW_at/\hbar)[(b|H+|a)\exp i(W_{ba}+E)t/\hbar +(b|H-|a)\exp i(W_{ba}-E)t/\hbar] \quad (55)$$

and assume for $\psi_1(a)$ a similar expansion. The coefficients are then determined to satisfy (54) and the initial condition. The result is

$$\psi_1(a)=(1/2)\sum_b\psi(b)\exp(-iW_at/\hbar) \times\left[\frac{(b|H+|a)(\exp[i(W_{ba}+E)t/\hbar]-1)}{W_{ba}+E} +\frac{(b|H-|a)(\exp[i(W_{ba}-E)t/\hbar]-1)}{(W_{ba}-E)}\right]. \quad (56)$$

Here $W_{ba}=W_b-W_a$ and the coefficients in (55) are given explicitly by

$$(b|H\pm|a)=\int\bar{\psi}(b)\Big(\sum_i(e/mc)\mathbf{p}_i \times\exp(\pm i\mathbf{k}\cdot\mathbf{r}_iE/hc)\psi(a)\cdot\mathbf{A} \mp\frac{iE}{hc}\int\bar{\psi}(b)\Big(\sum_i(e/mc)\mathbf{S}_i\Big)\psi(a)\cdot(\mathbf{k}\times\mathbf{A}), \quad (57)$$

in which $\bar{A}$ is to be written for $\mathbf{A}$ when the lower sign is used, the retardation of the wave has been neglected in the smaller spin term of the third line, and $\int$ means the usual integration over the entire configuration space involved in calculating matrix components.

In (56) if $W_{ba}>0$ as is the case in absorption only the term in $(b|H-|a)$ is important owing to the resonance denominator. Assuming E almost equal to W_{ba} so $W_{ba}-E=\Delta$, a small quantity one may write

[12] Cotton, Ann. chim. phys. **8**, 347 (1896).
[13] Schrödinger, Ann. d. Physik **81**, 109 (1926); Slater, Proc. Nat. Acad. **13**, 7 (1927); Pauling and Wilson, *Quantum Mechanics*, p. 302.
[14] Dirac, Proc. Roy. Soc. **A112**, 661 (1926); **A114**, 243 (1927); or *Quantum Mechanics*, second edition, Chap. XI.

$$\psi_1(a)=(1/2)\psi(b)\exp\left[-iW_bt/\hbar\right)$$
$$\times\frac{(b|H-|a)\sin\Delta t/2\hbar}{\Delta}\cdot 2i\exp(i\Delta t/2\hbar).$$

The probability that the molecule is in state b at time t is given by the absolute square of the coefficient of $\psi(b)$ in $\psi_1(a)$. The transition probability therefore is

$$P(a\rightarrow b)=|(b|H-|a)|^2\frac{\sin^2\Delta t/2\hbar}{(\Delta t/2\hbar)^2}\cdot\left(\frac{t}{2\hbar}\right)^2. \quad (58)$$

This is exactly the same as in the usual theory where the retardation of the light wave is neglected. Hence there is no need to repeat the standard treatment of (58) here. The next step is to consider $(b|H-|a)$ more closely. By expanding the exponential function in (57) and saving only the first two terms this can be written

$$(b|H-|a)=(i/\hbar c)W_{ba}(b|\mathbf{p}|a)\cdot\bar{A}-\frac{EW_{ba}}{2\hbar^2c^2}\mathbf{k}$$
$$\cdot(b|\mathbf{N}|a)\cdot\bar{A}+(iE/\hbar c)(b|\mathbf{m}|a)\cdot(\mathbf{k}\times\bar{A}), \quad (59)$$

in which $\mathbf{p}$ and $\mathbf{m}$ are electric and magnetic dipole moments as in section 1 and $\mathbf{N}$ is the electric quadrupole moment. The quadrupole moment term may be neglected for present purposes as it contributes nothing to circular dichroism. Neglecting the quadrupole moment term we see from (59) that the reduction of (58) will proceed exactly as in the usual theory except that $(b|\mathbf{p}|a)\cdot\bar{A}$ will be replaced by

$$(b|\mathbf{p}|a)\cdot\bar{A}+(E/W_{ba})(b|\mathbf{m}|a)\cdot(\mathbf{k}\times\bar{A}). \quad (60)$$

As the square of the magnitude of $(b|H-|a)$ appears in (58) this means that in place of $|(b|\mathbf{p}|a)\cdot\bar{A}|^2$ in the usual discussion we have here

$$|(b|\mathbf{p}|a)\cdot\bar{A}|^2+2(E/W_{ba})R$$
$$\times\{\mathbf{A}\cdot(a|\mathbf{p}|b)(b|\mathbf{m}|a)\cdot(\mathbf{k}\times\bar{A})\}. \quad (61)$$

We have now to consider the average of this over all orientations of the molecules. For brevity write $\mathbf{P}=(a|\mathbf{p}|b)$ and $\mathbf{M}=(b|\mathbf{m}|a)$ in the following calculations. The first term is

$$|\mathbf{P}\cdot\mathbf{A}|^2=|(\mathbf{P}_1+i\mathbf{P}_2)\cdot(\mathbf{A}_1+i\mathbf{A}_2)|^2$$
$$=(\mathbf{P}_1\cdot\mathbf{A}_1)^2+(\mathbf{P}_1\cdot\mathbf{A}_2)^2+(\mathbf{P}_2\cdot\mathbf{A}_1)^2$$
$$+(\mathbf{P}_2\cdot\mathbf{A}_2)^2+(\mathbf{P}_1\cdot\mathbf{A}_1\mathbf{P}_2\cdot\mathbf{A}_2+\mathbf{P}_2\cdot\mathbf{A}_1\mathbf{P}_1\cdot\mathbf{A}_2). \quad (62)$$

The average of $(\mathbf{P}_1\cdot\mathbf{A}_1)^2$ over all orientations of P_1 is $(1/3)P_1^2A_1^2$ and similarly for the other three terms of this form. For the last two terms in (62) we use the identity

$$\mathbf{P}_1\cdot\mathbf{A}_1\mathbf{P}_2\cdot\mathbf{A}_2+\mathbf{P}_2\cdot\mathbf{A}_1\mathbf{P}_1\cdot\mathbf{A}_2=(\mathbf{P}_1\times\mathbf{P}_2)\cdot(\mathbf{A}_1\times\mathbf{A}_2).$$

Averaging over all directions for $\mathbf{P}_1$ and $\mathbf{P}_2$ with a fixed angle between them amounts to averaging over all directions of $(\mathbf{P}_1\times\mathbf{P}_2)$ so the term on the right vanishes. Hence on averaging the last two terms of (62) cancel so the first term of (61) can be written

$$(1/3)|(b|\mathbf{p}|a)|^2|\mathbf{A}|^2.$$

The second term of (61) can be averaged as follows: the dyad $\mathbf{PM}$ multiplied into $(\mathbf{k}\times\bar{A})$ gives a vector along $\mathbf{P}$ which when averaged over all values of $\mathbf{P}$ making the fixed angle with $\mathbf{M}$ gives a vector along $\mathbf{M}$ of amount $\mathbf{P}\cdot\mathbf{M}_0\mathbf{M}\cdot(\mathbf{k}\times\bar{A})$ where $\mathbf{M}_0$ is a unit vector in the direction of $\mathbf{M}$. When this is averaged over all values of $\mathbf{M}$ which make a fixed angle with $(\mathbf{k}\times\bar{A})$ the result is a vector along $(\mathbf{k}\times\bar{A})$ of magnitude $\mathbf{P}\cdot\mathbf{M}\cos^2\theta$ where θ is the angle between $\mathbf{M}$ and $(\mathbf{k}\times\bar{A})$. Averaging over all values of θ one has Avge $[\cos^2\theta]=\frac{1}{3}$ so the average of $\mathbf{PM}\cdot(\mathbf{k}\times\bar{A})$ is a vector of magnitude $\frac{1}{3}\mathbf{P}\cdot\mathbf{Mk}\times\bar{A}$ hence the average obtained is

$$\text{Avge}\{\mathbf{A}\cdot\mathbf{PM}\cdot(\mathbf{k}\times\bar{A})\}=(1/3)\mathbf{P}\cdot\mathbf{MA}\cdot(k\times\bar{A}).$$

Now writing $\mathbf{A}=\mathbf{A}_1+i\mathbf{A}_2$ one has

$$\mathbf{A}\cdot(\mathbf{k}\times\bar{A})=i[A_2\cdot(\mathbf{k}\times\mathbf{A}_1)-A_1\cdot(k\times A_2)],$$

so this factor is pure imaginary and therefore on taking the real part as needed for the second term of (61) only the imaginary part of $\mathbf{P}\cdot\mathbf{M}$ will come in. In particular if the wave traveling in the $\mathbf{k}$ direction is circularly polarized then

$$\mathbf{A}=(1/\sqrt{2})A(\mathbf{i}\pm i\mathbf{j}), \quad (63)$$

where A is a real amplitude and where the upper sign represents right, the lower left circularly polarized light. For this one has

$$\mathbf{A}=(\mathbf{k}\times\bar{A})=\pm iA^2.$$

Hence finally the averaged form of (61) can be written

$$(1/3)A^2[|(b|\mathbf{p}|a)|^2 \mp 2(E/W_{ba})\mathrm{Im}\{(a|\mathbf{p}|b)\cdot(b|\mathbf{m}|a)\}], \quad (64)$$

where the upper sign applies for right, the lower for left circularly polarized light.

Hence the mean absorption transition probability ϵ will be the same as when retardation is neglected. But the difference between the two kinds will be in the following ratio to the mean

$$\frac{\epsilon_l-\epsilon_r}{\epsilon}=4\cdot\frac{\nu}{\nu_{ba}}\cdot\frac{\mathrm{Im}\{(a|\mathbf{p}|b)\cdot(b|\mathbf{m}|a)\}}{|(b|\mathbf{p}|a)|^2}, \quad (65)$$

in which ϵ_l and ϵ_r are written for the absorption transition probability for right and left circularly polarized light respectively.

These calculations provide the quantum-mechanical proof of Natanson's rule[15] previously obtained by classical methods. The rule is: if an absorption band absorbs left-circularly polarized light more strongly than right, then it contributes dextro-rotation to the medium for frequencies lower than that of the absorption band.

The results follow by comparing (65) with a combination of (7) and (10) resulting from elimination of β.

8. Rotatory Strength and Anisotropy Factor

In numerical discussions of the rotatory dispersion formula it is convenient to have a handy measure of the contribution of a given band to the rotatory power. For the absorption line $a\rightarrow b$ this is measured by

$$R(b,a)=\mathrm{Im}\{(a|\mathbf{p}|b)\cdot(b|\mathbf{m}|a)\}\cdot \quad (66)$$

where we shall call $R(b, a)$ the rotational strength of the line $a\rightarrow b$. It has the same dimensions as the ordinary line strength,[16] $(a|\mathbf{p}|b)^2$. It will be convenient to measure $R(b, a)$ in atomic units, that is, to measure $\mathbf{p}$ in units of ea where a is the radius of the first Bohr orbit, and $\mathbf{m}$ in Bohr magnetons. Both of these units are rather large for the quantities to be measured so we shall expect $R\ll 1$ in general.

Conventionally φ is given in degrees/decimeter and what is conventionally called the molecular rotatory power M is

$$[M]=(\varphi/\rho)M/100, \quad (67)$$

where φ is in degrees per decimeter, ρ is in gram/cm^3 and M is the molecular weight. Hence the connection between $[M]$ and Φ is

$$[M]=(18/\pi)\Phi \quad (68)$$

so, combining (8) and (10) one has

$$\frac{[M]}{(1/3)(n^2+2)}=24N(\hbar/\mu c)^2\sum_b\frac{R_{ba}\nu^2}{\nu_{ba}^2-\nu^2}. \quad (69)$$

Here R_{ba} is expressed in atomic units. The coefficient in (69) has the numerical value

$$24N(\hbar/\mu c)^2=21{,}700. \quad (70)$$

It is easy to calculate the value of the rotatory strength of an absorption band from the dispersion data as usually given by using (69) and (70). As an example consider Hunter's data[17] on *d*-sec-octyl alcohol. This extends from λ6708 to λ3650 and is represented by

$$[M]=\frac{4.08}{\lambda^2-0.0283},$$

where λ is in microns. Hunter has measured the refractive index n and from his data we find that $(1/3)(n^2+2)$ is 1.34 at λ6438 and 1.36 at λ3650 so this factor is essentially equal to 1.35 throughout the range. One has therefore

$$\frac{[M]}{(1/3)(n^2+2)}=\frac{3.02}{\lambda^2-0.0283}=\frac{106.9\sigma^2}{35.4-\sigma^2},$$

where σ is the wave number in reciprocal microns. Hence comparing with (69) one has that the main absorption band is at λ1680 and the strength of this is

$$R_{ba}=106.9/21{,}700=4.92\times10^{-3}.$$

In this way it is easy to calculate the rotatory strengths of the absorption lines when a rotatory dispersion formula is given.

Kuhn[18] has introduced another way of describing the rotatory strength of an absorption band by means of what he calls the anisotropy factor. Although the definitions he gives are in terms

[15] Natanson, J. de phys. **8**, 321 (1909).
[16] Condon and Shortley, *The Theory of Atomic Spectra* (Cambridge, 1935), p. 98.
[17] Hunter, J. Chem. Soc. **123**, 1671 (1923).
[18] Kuhn, Trans. Faraday Soc. **26**, 300 (1930).

of his coupled oscillator model it is readily seen that they amount to the following: the oscillator strength of the absorption line ν_{ba} is defined as the dimensionless number

$$f(b, a) = (8\pi^2\mu/3e^2h)\nu_{ba}|(a|\mathbf{p}|b)|^2. \quad (71)$$

Then Kuhn defines the anisotropy factor $g(b, a)$ for this line as

$$g(b, a) = \mathrm{Im}\{(a|\mathbf{p}|b)\cdot(b|\mathbf{m}|a)\}/|(a|\mathbf{p}|b)|^2. \quad (72)$$

The relation of Kuhn's anisotropy factor to our rotatory strength is then

$$f(b, a)g(b, a) = (2\pi/3)(a/\lambda_{ba})R(b, a), \quad (73)$$

in which $R(b, a)$ is expressed in atomic units, a is the radius of the first Bohr orbit and λ_{ba} is the wave-length of the absorption line $a \rightarrow b$. Thus the product fg is generally smaller by a factor of one to three thousand than the rotatory strength $R(b, a)$.

9. The Contribution of Spins to Optical Rotation

If a molecule contains an even number, $2n$, of valence electrons they can be paired in $(2n)!/n!2^n$ ways to give this number of distinguishable singlet bond eigenfunctions corresponding to each particular electronic configuration. To the very good approximation that the various operators for spin commute with the energy operator (i.e., neglecting magnetic interactions which are responsible in atoms for the fine structure) we can write down a bond function

$$B_i = \frac{1}{((2n)!)^{\frac{1}{2}}}\sum \pm P[\varphi_i(x_1y_1z_1\cdots z_n)\cdot \prod_{\substack{\text{all bond}\\ \text{pairs}}}(\alpha_i\beta_j - \alpha_j\beta_i)]$$

for each one of the $(2n)!/n!2^n$ ways of choosing the n bonds. Here φ_i is a function of space coordinates only and

$$\prod_{\substack{\text{all bond}\\ \text{pairs}}}(\alpha_i\beta_j - \alpha_j\beta_i) \equiv g_i$$

of spins alone. The antisymmetrizing operator $\Sigma \pm P$ indicates summation over all permutations of the electrons in the product $\varphi_i g_i$ taking the positive sign for even and the minus sign for odd permutations. This antisymmetric B_i satisfies the Pauli principle. Of these singlet bond functions only $(2n)!/n!(n+1)!$ are linearly independent. Now the lowest energy state of molecules having an even number of electrons is always a singlet so that the expression for optical activity will involve the term

$$\mathrm{Im}\sum_{n'}(n|\mathbf{r}|n')\cdot(n'|\mathbf{L}+2\mathbf{S}|n),$$

where n indicates the singlet bond function B_n which therefore satisfies the equation

$$\mathbf{S}^2B_n = 0B_n = \bar{S}_xS_xB_n + \bar{S}_yS_yB_n + \bar{S}_zS_zB_n.$$

Since each term after the last equality is zero or positive, each must be zero, so that $2(\mathbf{i}S_x + \mathbf{j}S_y + \mathbf{k}S_z)B_n = 0$. Thus spin will not contribute to the optical activity of unexcited molecules containing an even number of electrons. Since it is never possible to obtain excited molecules in sufficient amounts to contribute to optical activity, even if the spin were effective, the spin from such molecules never need be considered.

Next consider the case where there are $2n-1$ electrons, n still being an integer. Actual examples are provided by free radicals. States of lowest energy as before correspond to maximum electron pairing. Corresponding to each of the B_i functions for $2n$ electrons we now have a bond function

$$B_i' = (1/[(n-1)!]^{\frac{1}{2}})\sum \pm P[\varphi_i'(x_1\cdots z_{n-1})\cdot\alpha_k \prod_{\substack{\text{over}\\ n-1\\ \text{bond pairs}}}(\alpha_i\beta_j - \alpha_j\beta_i)]$$

which contains one unpaired electron and therefore satisfies the equation $S_zB_i' = (h/4\pi)B_i'$. Still another set B'' which satisfy the equation $S_zB'' = -(h/4\pi)B_i''$ is obtained by replacing α_k by β_k in each B_i'. Again consider the quantity $\mathrm{Im}\{\Sigma(n|\mathbf{r}|n')\cdot(n'|\mathbf{L}+2\mathbf{S}|n)\}$. Now

$$\begin{aligned}2\mathbf{S}B_{n'} &= 2(\mathbf{i}S_x + \mathbf{j}S_y + \mathbf{k}S_z)B_{n'}\\ &= (1/[(n-1)]^{\frac{1}{2}}!)\sum \pm P[\varphi_{n'}(x_1\cdots z_{n-1})\\ &\quad\cdot 2(\mathbf{i}\beta_k + \mathbf{j}(i\beta_k) + \mathbf{k}\alpha_k) \prod_{\substack{\text{over}\\ n-1\\ \text{bond pairs}}}(\alpha_i\beta_j - \alpha_j\beta_i)].\end{aligned}$$

Thus if both $B'_{n'}$ and

$$B_n' \text{ are real } (n'|2\mathbf{S}|n) \equiv \int \sum_{\substack{\text{spin}\\ \text{space}}} B'_{n'}2\mathbf{S}B_n'd\tau$$

contains an imaginary term only if in B_n' and $B'_{n'}$ the odd electron is assigned to an α state in one eigenfunction and a β state in the other; but in this case $(n|\mathbf{r}|n')$ is zero because of this difference in spin of the odd electron in the initial and final states.

The only way then that

$$\mathrm{Im}\{\Sigma(n|\mathbf{r}|n')\cdot(n'|2\mathbf{S}|n)\}$$

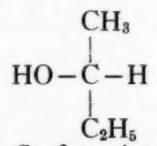
can be different from zero (for real eigenfunctions) would be for $\mathrm{Im}(n|\mathbf{r}|n')$ to be different from zero for the transition but this is impossible. However, suppose B_n' or $B'_{n'}$ contains an imaginary part. Since the operator H is real both the real and imaginary parts of any complex B_j' is separately an eigenfunction of H as one sees immediately by equating both the real and imaginary part of the corresponding Schrödinger equation to zero. There is therefore no loss in generality in assuming all B's to be either purely real or purely imaginary functions. Suppose now one of the B's is imaginary then the preceding argument about $\mathrm{Im}\{(n|\mathbf{r}|n')\cdot(n'|2\mathbf{S}|n)\}$ being zero can be taken over completely since the only effect is to multiply the result for real eigenfunctions by -1. Similarly if both eigenfunctions are imaginary the only effect is to multiply them by $+1$. Thus we have shown that to the approximation in which magnetic terms in the energy can be neglected the spins do not contribute to optical activity.

It follows from the above formulations and from the fact that $\mathbf{r}$ and $\mathbf{L}$ are each the sums of terms involving only one electron that exactly the same value is obtained for the optical activity when the φ's are used to calculate the matrices for $\mathbf{r}$ and $\mathbf{L}$ as when the antisymmetric B's are used. This is an important simplification. It is useful to make one further simplification which is justified by the observation that most transitions are satisfactorily described as single rather than multiple electron jumps. Thus we write $\varphi(x_1 \cdots z_n)=\psi_1(x_1y_1z_1)\psi_2(x_2 \cdots z_n)$ where $\psi_2(x_2 \cdots z_n)$ is unchanged in the transition and so can be integrated out before calculating the matrix components for $\mathbf{r}$ and $\mathbf{L}$. It is this approximation which forms the basis of our present treatment.

10. The Absolute Configuration of Secondary Butyl Alcohol

The procedure which we have applied to methyl phenyl carbinol nitrite leads to a definite statement for the absolute configuration of any molecule where the charge distribution about the chromophoric electron is known. Where the total rotatory power can be analyzed into the contribution from the different chromophoric electrons the theory provides a way of checking the assigned structure since a single assignment of charge distribution must give correctly the optical activity of all the different chromophoric electrons of the molecules. Such crucial tests will help to establish the range of validity of the present theory.

At least three determinations of the absolute configuration of butyl alcohol have been published. We indicate the configuration of butyl alcohol by the structural formula



Configuration (*I*)

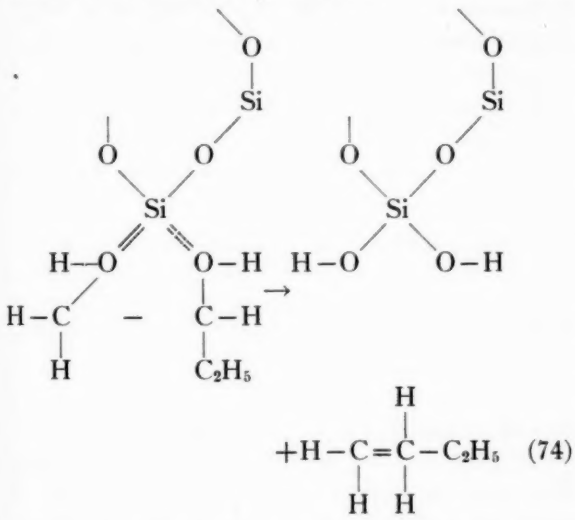
where the full lines indicate that H and OH lie in the plane of the paper and the dotted lines joining CH_3 and C_2H_5 to C indicate these groups lie below the plane of the paper. Boys'[19] rule applied to this configuration leads to the dextro-rotatory assignment. Kuhn[20] on the other hand using the theory of coupled oscillators comes to the conclusion that this isomer is laevo-rotatory. Finally Kirkwood,[21] concludes this isomer is dextro-rotatory in agreement with Boys.

While we shall use our theory to calculate the absolute configuration of secondary butyl alcohol it is of interest to consider another method of obtaining this same information. Schwab, Rost and Rudolph[22] report that dextro-rotatory quartz partially covered with copper or nickel provides a catalyst which dehydrates laevo-rotatory secondary butyl alcohol faster than the dextro-

[19] Boys, Proc. Roy. Soc. **A144**, 655 (1934).
[20] Kuhn, Zeits. f. physik. Chemie **B31**, 18 (1935).
[21] Kirkwood, J. Chem. Phys. **5**, 479 (1937).
[22] Schwab, Rost and Rudolph, Kolloid Zeits. **63**, 157 (1934).

rotatory form. Now quartz is known to crystallize in the form of spirals in which silicon and oxygen atoms alternate. Each spiral is connected with neighboring spirals since each silicon is bound to 4 oxygens and each oxygen to two silicons. Now there are right- and left-hand quartz spirals and they rotate plane polarized light in opposite directions. If some means can be devised to determine the absolute configuration of quartz, then as we shall see, a proper interpretation of experiments such as those of Schwab, Rost and Rudolph will fix the absolute configuration of secondary butyl alcohol.

First suppose that when water is removed from secondary butyl alcohol[23] the reaction may be represented as follows:



(74)

Suppose further that the butyl alcohol reacting belongs to configuration (*I*). Then as viewed normal to a plane passing simultaneously through the reacting H and OH and through the two carbon atoms to which these atoms are attached the molecule has the properties of a left-hand screw, since the ethyl group occupies more space than the hydrogen attached to the same carbon atom. If as we now explicitly assume there is an increased activation energy due to the steric hindrance of nonreacting groups then such a left-hand screw alcohol should react faster with right-hand quartz since screws of unlike sense fit along side of each other better than like screws. Such a consideration relates the configuration of the alcohol to that of the quartz. Two different methods for arriving at the absolute configuration of macroscopic hemihedral crystals such as quartz can be suggested. (1) As Pasteur demonstrated long ago it is frequently possible to pick out the two kinds of optically active crystals by the fact that different faces are developed on the two kind of crystals. The identification is then completed if crystal faces can be related to the structure of the crystal. Thus this problem resolves itself into an investigation of the factors responsible for the growth of crystal faces and avoids optical theory entirely in establishing absolute configuration. Such a method could of course be applied to any optically active crystal such as the tartrates thus avoiding uncertainties in deducing relative configurations. We now consider the second method.

(2) Optical theory can be applied directly to the crystal to deduce its absolute configuration. We leave to a future time the application of the present theory to quartz and accept provisionally Hylleraas'[24] application of the Born coupled oscillator theory in which he finds that right spiraling β-quartz is dextro-rotatory. Assuming this same relation holds for the slightly different low temperature α-quartz we are led by using our other considerations to the decidedly provisional result that laevo-rotatory butyl alcohol has configuration (*I*). This would be in agreement with Kuhn. While this result must be regarded as purely tentative it seems of very considerable interest to develop further both theoretically and experimentally this approach to absolute configuration because of the light it throws on surface reactions and optically active synthesis.

We now examine in more detail some of the steps in the preceding argument. Suppose that the dehydration of configuration (*I*) actually results in the formation of a double bond between the second and third carbon atoms instead of 1–2 butylene as we first supposed. Examination of the model shows that this can occur by the OH giving off with either of the two hydrogens on the third carbon atom. In the mechanism we will call (1) the four carbon atoms will lie in a plane so that such a molecule

[23] Schwab, Rost and Rudolph imply that the butylene formed from the dehydration of secondary butyl alcohol has the double bond in the 1,2 position but do not say they have investigated this point.

[24] Hylleraas, Zeits. f. Physik **44**, 871 (1927).

would react equally well with either right or left quartz. Thus whatever part of the reaction goes this way cannot be responsible for the observed differential rate and is therefore not interesting for optical activity. It is very likely that steric repulsions between the hydrogens on the end carbon atoms are responsible for reducing the importance of this mechanism. The product of such a mechanism would be 2–3 *cis* butylene.

By mechanism (2) 2–3 *trans* butylene will be the product and configuration (*I*) can be seen, by examining a model to behave like a right screw so that by our former assumption, of fastest reaction between unlike screws, it should go fastest on left spiraling quartz. Thus if 2–3 *trans* butylene (and not 1–2 butylene) is the chief decomposition product in the Schwab, Rost and Rudolph experiment then keeping our tentative assignment of the absolute configuration of quartz we would conclude that configuration (*I*) is the dextro form.

The preceding discussion then suggests that experiments designed to answer the following questions will be particularly valuable.

(1) Is the product of dehydration of secondary butyl alcohol 1–2 or 2–3 butylene and, if the latter, is it *cis* or *trans?*

(2) What is the function of the metal in the dehydration?

(3) Is the rate of dehydration of the secondary alcohol slowed down by replacing nonreacting radicals in the molecule by larger substituents?

From the point of view of the catalytic theory it is particularly significant that the spiral character of quartz in bulk still persists in the surface layer.

We have made a provisional calculation of the rotatory power of butyl alcohol considering only the contribution from the hydroxyl as chromophoric group. The configuration adopted is that of (*I*), the carbon atoms are numbered in order along the chain with the OH group on C_2. Hydrogen atoms 0 and 1 are on C_1, 3 is on C_2, 4 and 5 are on C_3 and 6, 7, 8 on C_4 while H_9 is the hydrogen of the hydroxyl group. The assumed coordinates of the atoms are given in Table II. Here the coordinates are given in angstrom units. The charges assumed for the atoms are (in 10^{-10} e.s.u.): given in the last line of the table. This set of charges and coordinates determines the principal axes of the quadratic potential terms in accordance with the following linear transformation

$$u=-0.9797x+0.510y\ +0.1939z,$$
$$v=+0.0015x-0.9691y+0.2465z,$$
$$w=+0.1999x+0.2398y+0.9498z,$$

in terms of which it is found that the dissymmetry coefficient has the value, $A=2.8153\cdot 10^{10}$. If the unperturbed force constant is chosen so that the longest wave-length absorption band is at 1620A (this is the critical frequency in the empirical one-term dispersion formula) the three calculated frequencies associated with the three axes become,

$$\nu_u=2.3873\cdot 10^{15}, \qquad \nu_v=1.8518\cdot 10^{15},$$
$$\nu_w=2.2568\cdot 10^{15}.$$

These lead to a theoretical value of the parameter β which is

$$\beta=3.644\cdot 10^{-38}$$

as the contribution of the hydroxyl group to rotatory power at the NaD line wave-length. The experimental value of β calculated from the observed rotatory power by means of (6) is $\beta=1.40\cdot 10^{-35}$. This value of course includes the contribution from all electrons and is the average effect allowing for all configurations assumed under conditions of more or less free rotation about the bond axes. The large discrepancy may of course mean that the one-electron model is of secondary importance in this case. On the other hand other possible configurations and assumptions concerning the unperturbed state would give a much more favorable result. Thus a

TABLE II.

	O	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	H_0	C_1	C_2	C_3	C_4
x	0	+1.85	+0.96	+1.85	−0.92	+0.92	−0.92	+0.92	0	0	−0.92	+1.24	0	0	0
y	0	−1.08	−1.60	−0.04	+1.60	+1.60	+3.05	+3.05	+1.85	−0.94	−0.53	−0.77	0	+1.43	+2.40
z	0	−1.08	−2.55	−2.55	−2.55	−2.55	−0.78	−0.78	+0.18	+0.24	−1.80	−1.94	−1.42	−1.94	−0.76
e	−2.16	all hydrogens +0.28										−0.84	+0.32	−0.56	−0.84

moderate change in the difference between ν_u and ν_w would introduce a power of ten and a more favorable relation of the principal axes would help very much. We shall consider these possibilities more fully at a later time.

11. Other Consequences of the Theory

The known dipoles of various bonds lead us to locate charges on the atoms from which we can calculate the contribution to the potential coming from these coulomb forces. Other contributions toward rotatory power will arise from the coupling of the chromophoric electron with other electrons in the molecule. It is this latter effect which in the past has been considered to the complete exclusion of other mechanisms. Wherever charges are present both mechanisms undoubtedly contribute to the total effect.

Empirically it has been known[25] for some time that there is a relationship between total dipole moment and optical activity. Furthermore Rule[26] has attempted to relate optical activity to the constituent moments particularly with respect to their size and propinquity to the optically active carbon atom. From the theory presented here we are compelled to postulate the existence of such relationships in a definite quantitative way. Particularly large effects are to be expected wherever the chromophoric electron is closely and asymmetrically surrounded by ions such as are found in ionic crystals (quartz, cobaltioxalate crystals, etc.) Another effect the quantitative treatment of which falls naturally within the scope of this approach is the large change caused by polar and polarizable solvents on rotatory power. This effect interpreted in accord with the present formulation makes it possible to apply optical activity in a quantitative way to the study of liquid structure. As Wolf and Volkmann,[27] Beckmann and Cohen[28] and others have pointed out it is due to the electric forces originating from solvent dipoles surrounding the active molecules. We now readily understand that such forces will change the potential in which the chromophoric electron is moving without having to postulate, as Beckmann and Cohen do, an actual distortion of the molecular frame.

A polar solvent tends to form a compound with highly charged parts of the optically active molecule; in so doing it partially neutralizes these charges thereby reducing the rotatory power. Thus the general effect of polar solvents should be to lower optical activity except in special cases where enhancement results from neutralization of charges which were themselves previously acting to lower the optical activity. These expectations are born out by experiment.[29]

Comparatively small changes in charge distribution may in fact lead to large changes or even reversal of sign of the asymmetry coefficient A. Thus when the shape of the molecule is not rigidly fixed the over-all rotatory power of the compound will show great sensitivity to all factors which modify the statistical weight of particular configurations. The classical example for this is furnished by tartaric acid and its salts and esters where free rotation about single bonds is restricted by steric effects and compound formation. This results in the well-known temperature and concentration anomaly.

Our thesis that any dispersion electron is made optically active whenever it is brought into a dissymmetric field provides a clear explanation of "induced optical activity" in the sense discussed by Lowry in cases where the dispersion electron is not directly attached to an asymmetric center. The carbonyl group in sugars is a striking example of this possibility. In such a case as this the asymmetric influence cannot be transmitted by way of bonds so that the conclusion seems inescapable that the effect is a coulombic one transmitted through space.

[25] Betti, Trans. Faraday Soc. **26**, 227 (1930).
[26] See Lowry, *Optical Rotatory Power*, pp. 326 *et seq.*
[27] Zeits. f. physik. Chemie **B3**, 139 (1929).
[28] Beckmann and Cohen, J. Chem. Phys. **4**, 784 (1936).
[29] Lowry, *Optical Rotatory Power* (Longmans Green 1936), p. 350.

Absorbing and Reflecting Powers of Electrolytes in the Far Infrared

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The absorbing and reflecting powers and the dispersion of different concentrations of HCl, LiCl, NaCl, KCl, KBr, LiI, KI, ZnI_2, $MgSO_4$, KOH and H_2SO_4 were measured in the spectral region of 50μ to 150μ. The results are discussed in terms of, (1) Maxwell's equations in which the inertia of the ions is included, (2) the influence of ions on the absorbing power of water molecules, (3) the electrical conductivity for high frequency electromagnetic fields, (4) the radius of ions, (5) the hydration of ions and (6) the validity of Stokes' law for the microscopic process involved.

INTRODUCTION

THE interaction between radiation and matter can be interpreted in terms of the displacements of electric charges. Although spectroscopy has been mainly concerned with the motion of bound charges and the application of quantum theory, there are important problems to be solved which deal with the translational motion of charges in an electromagnetic field. Probably the reason why spectroscopy has not turned to more of these problems is due to the experimental difficulties; namely, the necessity to measure absolute intensities rather than just the positions of eigenfrequencies, which often suffice for quantum theory problems. The experimental work on the translation of charges has been almost entirely limited to the movement of free electrons in metals under the action of infrared radiation and the movement of electrolytic ions due to static fields and short radio waves. In the present investigation, we have studied the motion of several ions under the influence of infrared radiation from 50μ to 150μ by determining the reflecting and absorbing powers and hence the dispersion of electrolytes. We will be concerned mainly with the following problems: (1) Under what conditions does the inertia of an ion become dominant in hindering its movement in an alternating electric field as the frequency is varied? (2) Are the ions bound in a quasicrystalline structure so that a characteristic frequency of oscillation exists which corresponds to the reststrahlen frequency of an ionic crystal? (3) What is the effective mass and radius of an ion in an electrolyte; or, how many water molecules are bound to an ion? (4) Do the anomalously high electrical conductivities of H^+ and OH^- ions and especially small electrical conductivities of Li^+ and Mg^{++} ions, as observed with a static field or radio waves, also occur under the influence of infrared radiation?

One difficulty in applying any theory to the motion of ions in an electrolyte is the value to be assigned to the intensity of the electric field; that is, the validity of the formula, $E=(n^2+2)F/3$, for determining the microscopic field about an ion from the macroscopic field that is measured. In this respect, measurements of conductivity with infrared radiation seem particularly favorable because the dielectric constant, $\epsilon=n^2$, is considerably smaller in the infrared than for radio waves or a static field and hence a smaller error should be introduced in calculating the effective field acting on an ion.

SIMPLE THEORY

We will assume that the motion of an ion in an electromagnetic field satisfies the equation:

$$mdv/dt+pv=eEe^{i\omega t}, \qquad (1)$$

where m is the mass of the ion of charge e, $Ee^{i\omega t}$ the intensity of the alternating field and p is the frictional force for unit velocity. The frictional force, p, partly takes account of forces existing between the ions and surrounding water molecules, but we will neglect any resonance phenomenon. The current, I, which is produced by the electric field is:

$$I=Zev=Ze^2Ee^{i\omega t}/p=\Lambda Ee^{i\omega t}, \qquad (2)$$

where Z is the number of ions per unit volume and Λ is the specific conductivity of the electro-

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lyte. Solving Eq. (1) under these conditions gives:

$$\Lambda = Ze^2/(p+i\omega m), \tag{3}$$

which shows that when

$$\nu_0 = c/\lambda_0 = \omega_0/2\pi = p/2\pi m, \tag{4}$$

the frictional force and the inertia of an ion are equally effective in hindering its motion in an alternating electric field of frequency ν_0 or wave-length λ_0. For longer wave-lengths, the inertia becomes less important. Using Stokes' law for the frictional force,

$$p = 6\pi\eta r, \tag{5}$$

where η is the viscosity of the electrolyte and r is the radius of the ion, Eq. (4) becomes

$$\lambda_0 = mc/3\eta r. \tag{6}$$

Assuming no water molecules to be tightly bound to the ions, inserting the usual values for m and r in Eq. (6) shows the order of magnitude of λ_0's to be $\lambda_{Cl^-} = 30\mu$, $\lambda_{K^+} = 50\mu$, $\lambda_{Br^-} = 70\mu$ and $\lambda_{I^-} = 100\mu$.

The electrical conductivity of the ions is determined from the absolute intensity of absorption; that is the proportion of the electromagnetic radiation that is converted into heat by the ions. Writing Maxwell's equation as

$$\left(\frac{i\omega\epsilon}{c} + \frac{4\pi\Lambda}{c}\right)Ee^{i\omega t} = \frac{i\omega}{c}\left(\epsilon - \frac{-i4\pi\Lambda}{\omega}\right)Ee^{i\omega t} = \text{Curl } He^{i\omega t}, \tag{7}$$

and using complex values for the dielectric constant, ϵ, and the index of refraction, n,

$$\bar{\epsilon} = \epsilon - i4\pi\Lambda/\omega = \bar{\eta}^2 = n^2(1-ia)^2 = n^2 - i4\pi\Lambda/\omega. \tag{8}$$

Equating imaginary terms in expression (8) using Eqs. (3) and (4) for Λ and ν_0 give:

$$n4\pi na\nu = (2Ze^2/m)[\nu_0/(\nu^2+\nu_0^2)], \tag{9}$$

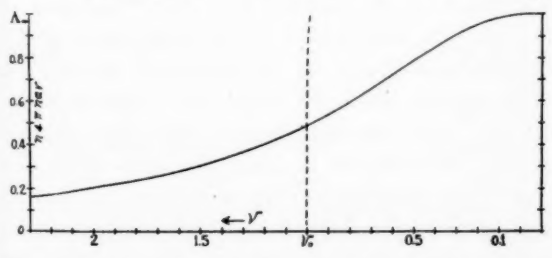

FIG. 1. Theoretical absorption of an ion as a function of wave-length.

where na is the absorption coefficient of an electrolyte due to the presence of ions and n is the index of refraction of the electrolyte for radiation of frequency ν. When $\nu \ll \nu_0$, $(\nu_0 = p/2\pi m)$,

$$n4\pi na\nu = 2Ze^2/m\nu_0 = 4\pi Ze^2/p = 2Ze^2/3\eta r, \tag{10}$$

where in the last expression, Stokes' law of friction $(p = 6\pi\eta r)$ is assumed. For a frequency $\nu = \nu_0$ the value of $n4\pi na\nu$ should be just half as great as given by Eq. (10).

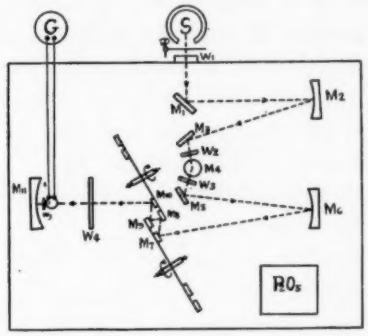

FIG. 2. Reststrahlen apparatus.

From Maxwell's equations it follows that the electrical conductivity is related to the absorption coefficient by the relation:

$$\Lambda = nna\nu. \tag{11}$$

In Fig. 1 is shown the electrical conductivity, obtained from Eqs. (9) and (11), due to a single kind of ion as a function of frequency. Naturally we must always deal with the simultaneous action of two kinds of ions for which the λ_0's are in general different and therefore the observed conductivity should be the sum of two curves as shown in Fig. 1.

APPARATUS AND EXPERIMENTAL CONDITIONS

Figure 2 shows schematically a top view of the reststrahlen apparatus used for obtaining monochromatic radiations of 52μ, 63μ, 83μ, 100μ, 117μ and 152μ. A small Auer gas mantle protected by a water-cooled envelope served as a source of radiation. The radiation was periodically interrupted by a shutter of NaCl which was only opaque to wave-lengths longer than 20μ. The radiation then entered an hermetically sealed box, in which the air was dried with P_2O_5, through a paraffin window, W_1, of 2 mm thickness and was reflected from mirror M_1 of

roughened aluminum. After being reflected from the spherical mirror M_2, the radiation was reflected downward at an angle of less than 10° to the vertical by a plane mirror M_3 and passed through a window of paraffin, W_2, of 1 mm thickness. The radiation was brought to a focus at M_4 where it was again reflected. It then proceeded by a symmetrical path through the paraffin window W_3 and was reflected by mirrors M_5 and M_6 to fall on the reststrahlen crystals M_7, M_8, M_9 and M_{10}. The radiation was finally condensed by mirror M_{11} on one receiver of a compensated thermocouple after it passed through a thin paraffin filter, W_4, and a window of crystalline quartz, W_5.

For reflection measurements, the liquids to be studied and a mirror of evaporated tin were mounted on a horizontal disk that could be rotated externally to bring a liquid surface or the tin mirror to position M_4. The reflection at M_4 occurred in a separate compartment that was sealed by the paraffin windows W_2 and W_3.

For transmission measurements, windows W_2 and W_3 were removed and the electrolyte contained between two plates of crystalline quartz, each 2 mm thick, was mounted between M_4 and M_5. By an external mechanism, the absorption cell could be replaced by a comparison plate of crystalline quartz 4 mm thick.

The reststrahlen crystals were all mounted on two large disks that could be turned externally so as to change the wave-length of the radiation. The vacuum thermocouple was constructed with bismuth alloy wires with two active junctions and two compensating junctions. Two types of receiving surfaces were tried with about equal success. For one pe, typowdered glass was put on the front of a thin gold receiver. For the other, thin glass with a back surface of evaporated gold was used. The main feature of the thermocouple was a very careful compensation for eliminating zero-drift. Besides constructing the active and compensating junctions and the receivers as nearly alike as possible, an added compensation was obtained by using a resistance across the more sensitive pair of junctions. Actually the drift was reduced by a factor of 1000 by the use of the compensating junctions instead of only the active ones and the size of the deflections were reduced only 40 percent. The galvanometer was of special construction with the moving system very carefully balanced. It had a period of 10 seconds and was mounted on a vibrationless support having internal damping. The galvanometer deflections were read by a parallel-plate optical amplifier which was constructed so that first-order drifts were automatically eliminated.

The essential features of our reststrahlen apparatus were the precautions taken to avoid impurities in the desired spectrum due to short wave-length radiation, the protection of the liquids studied from direct radiation from the source, the mechanical facilities for changing the liquids being measured for reflection and transmission, the mechanical means for changing the reststrahlen crystals in a dry atmosphere and the stability of the galvanometer readings. By measuring the transmission of NaCl when two metal mirrors replaced two reststrahlen crystals, it was estimated that less than 0.01 percent of the desired radiation was due to short wave radiation. The inaccuracy of the measurements was of the order of 1 percent for transmission and 0.1 percent for reflection. The best precision was obtained for 100μ for which the galvanometer deflection was about 130 mm for reflection from the tin mirror and about 65 mm for the transmission of the empty absorption cell. These values correspond to a scale at 5 m distance from the galvanometer; the average Brownian motion fluctuations amounted to about 0.1 mm for the galvanometer we used.

The reststrahlen crystals were of NaCl (52μ), KCl (63μ), KBr (83μ), TlCl (100μ), TlBr (117μ) and TlI (152μ). The average wave-length of the radiation obtained by the method of reststrahlen depends somewhat on the particular apparatus; since the actual radiation obtained depends on the energy distribution of the source, the absorption of the atmosphere, the roughness of the reflecting surfaces, and the absorption of the windows and filters. We determined the average wave-lengths obtained from our apparatus by measuring the transmission of crystalline quartz. In Fig. 3 is shown a curve for the absorbing power of crystalline quartz obtained with a grating spectrometer;[1] the short horizontal lines give the values obtained with the reststrahlen

[1] C. H. Cartwright, Zeits. f. Physik **90**, 480 (1934).

apparatus. Taking into account that when the absorbing power of a medium is changing as a function of wave-length, any lack of strict monochromacy produces an apparently smaller absorbing power, the values for the wave-lengths obtained agree well with the maxima reflecting powers of the salts. The reststrahlen radiation obtained from TlCl is usually taken as 92μ but in our case 100μ corresponds better to the absorption of crystalline quartz. This difference is not surprising when we consider that the reflecting powers of thallium salts are not nearly so well defined as for NaCl, KCl and KBr; this is illustrated by the dotted curves in Fig. 3.[2] The precautions we took to purify the spectrum of short wave-length radiation shifted the average wave-length from 92μ to 100μ after four reflections. The effectiveness of thallium salts for reststrahlen is however much greater than appears from the curve in Fig. 3 because the intensity of the radiation diminishes very rapidly with wave-length.

From the transmission measurements, the absorption coefficient, na, of an electrolyte was calculated for each wave-length by the usual formula:

$$I=I_0e^{-4\pi na d/\lambda}, \tag{12}$$

where I is the intensity of the radiation transmitted by the quartz cell containing a thickness d of an electrolyte and I_0 is the intensity transmitted by the comparison quartz plate. To account for the loss by reflection from the two surfaces quartz-liquid and liquid-quartz, I in Eq. (12) should be multiplied by a factor

$$\left\{1-\left(\frac{n_q-n}{n_q+n}\right)^2\right\}^2, \tag{13}$$

where n_q is the index of refraction for quartz and n that of the liquid. In Table I are given

TABLE I.

λ in μ	52	63	83	100	117	152
ν in cm^{-1}	192	159	120	100	85	66
n_q	2.26	2.22	2.19	2.18	2.17	2.16

the values of n_q for crystalline quartz as measured by Rubens.[3] As will be seen from the data to follow, the differences between n and n_q are sufficiently small for the electrolytes we studied to justify neglecting the factor (13). The reflections air-quartz and quartz-air as well as the

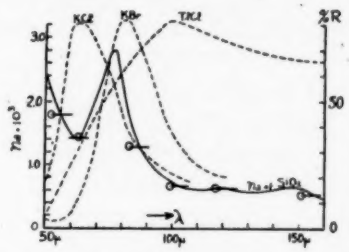

FIG. 3. Reststrahlen reflections and quartz absorption.

absorption by the quartz were taken into account in Eq. (12) by using the comparison quartz plate. Any multiple interference between the two surfaces of the electrolyte can be neglected because of the small reflection of liquid-quartz and the large absorption of the electrolyte. Multiple reflections between the outer quartz surfaces of the comparison cell can also be neglected due to the thickness of the quartz plates compared with the resolving power.[4]

The index of refraction of an electrolyte was determined from the reflecting power, R, and the absorption coefficient, na, by the usual formula,

$$R=\frac{(n-1)^2+n^2a^2}{(n+1)^2+n^2a^2}, \tag{14}$$

which can be rewritten to facilitate calculation as:

$$n=\frac{R+1}{R-1}=\left\{\left(\frac{R+1}{R-1}\right)^2-n^2a^2-1\right\}^{\frac{1}{2}}. \tag{15}$$

A technical difficulty occurred in measuring the absorption of electrolytes between 50μ and 100μ due to the strong absorption of water. Rather than rely on the thickness of about 20μ spacers between the quartz plates comprising the absorption cell or to measure the thickness of the electrolyte each time by interference methods, we determined the absorption coefficients of the electrolytes for a thickness of $d=34.6\mu$ at $\lambda=117\mu$ where the absorption coeffi-

[2] H. Rubens and H. V. Wartenberg, Berlin Ber. 69 (1914).
[3] H. Rubens, Berlin Ber. 556 (1917).
[4] C. H. Cartwright and M. Czerny, Zeits. f. Physik **85**, 269 (1933).

TABLE II.

H_2O

λ in μ	52	63	83	100	117	152
ν in cm^{-1}	192	159	120	100	85	66
% R (Average)	9.30	10.74	11.75	12.28	12.80	13.40
na (Average)	0.48	0.51	0.47	0.370	0.337	0.388
$4\pi na\nu$ in cm^{-1}	1160	1020	710	464	362	320
n (Average)	1.68	1.77	1.89	2.01	2.04	2.09

6 Normal HCl

% R	13.71	15.71	17.15	18.45	19.50	20.05
% Trans. (d = 34.6μ)					14.2	
% Trans. (d = 18.2μ)	7.5	8.0	20.5	28.5	35.7	40.0
na	0.59	0.70	0.58	0.545	0.526	0.607
n	1.94	2.01	2.17	2.35	2.45	2.44

3 Normal HCl

% R	11.37	—	—	15.70	17.12	17.90
% Trans. (d = 34.6μ)	—	—	—	—	19.1	—
na	—	—	—	—	0.446	—
n	—	—	—	—	2.31	—

6 Normal LiCl

% R	11.20	12.73	13.28	13.39	13.40	14.40
% Trans. (d = 38.2μ)					26.6	
% Trans. (d = 10.5μ)	33.7	37.0	52.0	63.4	69.3	73.7
na	0.43	0.48	0.41	0.345	0.324	0.353
n	1.87	1.96	2.04	2.08	2.09	2.15

3 Normal LiCl

% Trans. (d = 38.2μ)					26.0	
na					0.329	

5 Normal NaCl

% R	11.04	13.30	14.20	15.45	16.68	17.40
% Trans. (d = 38.2μ)					15.9	
% Trans. (d = 10.5μ)	23.5	26.9	40.1	51.4	60.0	64.8
% Trans. (d = 19.1μ)	6.5	10.0	19.4	29.3	39.7	45.9
na (Average)	0.58	0.61	0.57	0.510	0.450	0.496
n	1.73	1.89	2.01	2.14	2.27	2.30

2.5 Normal NaCl

% R	10.10	12.20	13.10	13.98	15.56	15.78
% Trans. (d = 38.2μ)					20.7	
% Trans. (d = 13.7μ)	19.4	21.4	35.2	47.9	56.8	62.0
% Trans. (d = 20.5μ)	10.1	11.8	22.2	32.9	43.0	48.4
na (Average)	0.48	0.55	0.50	0.430	0.385	0.426
n	1.74	1.86	1.98	2.00	2.22	2.22

3 Normal KCl

% R	9.30	10.91	12.42	13.55	14.32	14.83
% Trans. (d = 38.2μ)					15.8	
% Trans. (d = 9.1μ)	30.8	33.1	45.5	54.5	64.6	69.2
na	0.54	0.61	0.57	0.532	0.451	0.491
n	1.62	1.67	1.85	1.98	2.09	2.11

1.5 Normal KCl

% R	9.26	11.32	12.17	13.20	14.43	14.60
% Trans. (d = 38.2μ)					19.8	
% Trans. (d = 9.2μ)	33.4	35.2	50.0	62.5	67.7	70.6
na	0.49	0.57	0.50	0.406	0.395	0.457
n	1.66	1.76	1.90	2.03	2.13	2.11

4 Normal KBr

% R	8.28	10.82	11.90	13.78	15.00	16.05
% Trans. (d = 38.2μ)					15.6	
% Trans. (d = 8.9μ)	34.9	36.6	48.8	59.0	64.8	66.7
na	0.49	0.57	0.53	0.474	0.454	0.552
n	1.53	1.72	1.84	2.04	2.14	2.16

2 Normal KBr

% R	8.64	10.80	11.60	12.91	13.70	14.25
% Trans. (d = 38.2μ)					19.0	
% Trans. (d = 9.3μ)	34.1	37.0	49.2	61.5	66.5	70.0
na	0.48	0.54	0.50	0.418	0.406	0.465
n	1.62	1.75	1.85	2.01	2.07	2.08

6 Normal LiI

% R	9.95	10.72	12.08	13.39	14.86	16.01
% Trans. (d = 38.2μ)	4.4	4.6	6.1	13.4	19.4	21.9
% Trans. (d = 18.4μ)	20.2	22.0	27.5	38.6	45.3	49.2
na (Average)	0.36	0.41	0.47	0.416	0.401	0.475
n	1.82	1.85	1.92	2.05	2.16	2.22

3 Normal LiI

% Trans. (d = 38.2μ)					23.0	
na					0.359	

4 Normal KI

% R	8.40	8.53	9.97	11.78	13.48	15.41
% Trans. (d = 38.2μ)					16.4	
% Trans. (d = 12.8μ)	28.6	30.3	39.1	47.0	54.5	58.0
na	0.40	0.47	0.49	0.470	0.442	0.509
n	1.67	1.62	1.75	1.89	2.04	2.14

2 Normal KI

% Trans. (d = 38.2μ)					19.9	
na					0.394	

14.8 Normal ZnI_2

% Trans. (d = 38.2μ)					21.1	
na					0.380	

7.4 Normal ZnI_2

% R	10.82	12.14	12.70	13.49	14.68	15.31
% Trans. (d = 38.2μ)					24.5	
% Trans. (d = 20.9μ)	11.0	13.6	25.4	41.3	46.2	50.0
na	0.44	0.48	0.43	0.337	0.344	0.401
n	1.84	1.91	1.98	2.09	2.18	2.20

4 Normal $MgSO_4$

% R	12.00	13.25	13.48	13.94	14.20	14.60
% Trans. (d = 38.2μ)					29.8	
% Trans. (d = 19.5μ)	10.8	13.1	25.8	42.8	53.9	58.1
na	0.47	0.52	0.46	0.346	0.296	0.338
n	1.91	1.97	2.03	2.08	2.12	2.13

2 Normal $MgSO_4$

% Trans. (d = 38.2μ)					26.6	
na					0.324	

6 Normal KOH

% R	11.70	13.50	13.80	15.00	15.95	16.80
% Trans. (d = 34.6μ)					20.3	
% Trans. (d = 20.5μ)	7.2	9.2	20.0	31.1	38.8	42.5
na	0.53	0.58	0.52	0.455	0.430	0.507
n	1.83	1.93	2.01	2.14	2.23	2.25

3 Normal KOH

% R	10.73	—	—	13.60	14.51	15.45
% Trans. (d = 34.6μ)					25.2	
na					0.372	
n					2.15	

TABLE II (*Continued*).

2 Normal H_2SO_4						
% R	10.7	11.8	12.8	13.8	15.1	15.8
% Trans. ($d=34.6\mu$)					20.7	
% Trans. ($d=21.0\mu$)	7.0	8.5	15.5	29.2	38.5	44.0
na	0.53	0.59	0.59	0.47	0.42	0.47
n	1.75	1.78	1.87	2.07	2.17	2.19
6 Normal H_2SO_4						
% R	13.1	14.7	16.2	17.0	18.5	19.7
% Trans. ($d=34.6\mu$)					15.2	
% Trans. ($d=21.4\mu$)	3.7	4.7	13.0	23.5	31.2	35.2
na	0.64	0.72	0.63	0.54	0.51	0.59
n	1.85	1.88	2.11	2.27	2.38	2.42
12 Normal H_2SO_4						
% R	16.8	18.7	19.6	21.0	22.5	23.6
% Trans. ($d=34.6\mu$)					11.5	
% Trans. ($d=21.0\mu$)	2.0	3.2	10.3	18.8	26.9	29.9
na	0.77	0.82	0.71	0.63	0.58	0.70
n	2.02	2.13	2.33	2.53	2.66	2.69

cients change rather slowly with wave-length and the absorption coefficients are considerably less than for shorter wave-lengths where the broad water band occurs. Then a thinner spacer of platinum was used and its thickness was calculated by formula (12) by again measuring the transmission at $\lambda=117\mu$.

EXPERIMENTAL RESULTS

In Table II are recorded for the different reststrahlen frequencies, the reflecting power, R, the transmission of an electrolyte of thickness d, the absorption coefficient of the electrolyte, na, and the index of refraction, n.

DISCUSSION

1. Absorption of water

In order to apply Maxwell's equations to the movement of the ions in an electrolyte, it is necessary to subtract the effect of water from the observed quantities. As a first approximation, we shall make the *assumption* (*A*) that the absorbing power per molecule of water is the same in an electrolyte as in pure water; that is, we shall first calculate the absorption due to ions by the formula:

$$(na)_{\text{ions}}=(na)_{\text{mes.}}-(Cna)_{H_2O}, \qquad (16)$$

where the concentration, C, will be taken as the volume of water per volume of solution. This concentration as well as the results of other ways of calculating concentration is tabulated in Table III along with the viscosity and electrical conductivity measured in a static field.

In Fig. 4A are shown the values of $n4\pi na\nu$ (ν is expressed in cm^{-1}) for the ions only as calculated according to the assumption underlying Eq. (16).

To correct more accurately for the water absorption which unfortunately plays a great rôle, it is necessary to understand the causes for the absorption due to the water. In Fig. 5 is shown the absorption coefficient for liquid water and we can distinguish between two types of absorption: one type due to a broad absorption band and one type causing a regular increase in the absorption coefficient. The broad absorption band, as shown by other investigations,[5] can be attributed to intermolecular origin and we shall at first assume that this absorption is not altered by the presence of ions. The more general type of absorption is well accounted for by the Debye theory of dipole orientation for which

$$4\pi na\nu\eta=\text{constant}. \qquad (17)$$

We shall assume that at $\lambda=152\mu$ the water absorption is entirely due to the orientation of dipoles and this gives the constant (17) a value of 3.20 (ν is expressed in cm^{-1} and η for water is 0.01). In Fig. 4B are shown the values of the absorption due only to ions as calculated by the formula

$$(na)_{\text{ions}}=(na)_{\text{mes.}}-C[(na)_{H_2O}-(320/4\pi\nu)(1-1/\eta)], \qquad (18)$$

where for η we will take the viscosity of the electrolyte. In this formula we make the additional *assumption* (*B*), that the presence of ions does not alter the intensity of the broad absorption band in water but the absorption by the water molecules due to dipole orientation depends on the viscosity of the electrolyte. For electrolytes of high viscosity, the values in Fig. 4B differ considerably from those in Fig. 4A and the absorption as a function of wave-length, even allowing for inaccuracies, is in general much different from the addition of two curves of the type shown in Fig. 1. Most of the curves in Fig. 4A and 4B indicate that the presence of

[5] C. H. Cartwright, Nature **136**, 181 (1935).

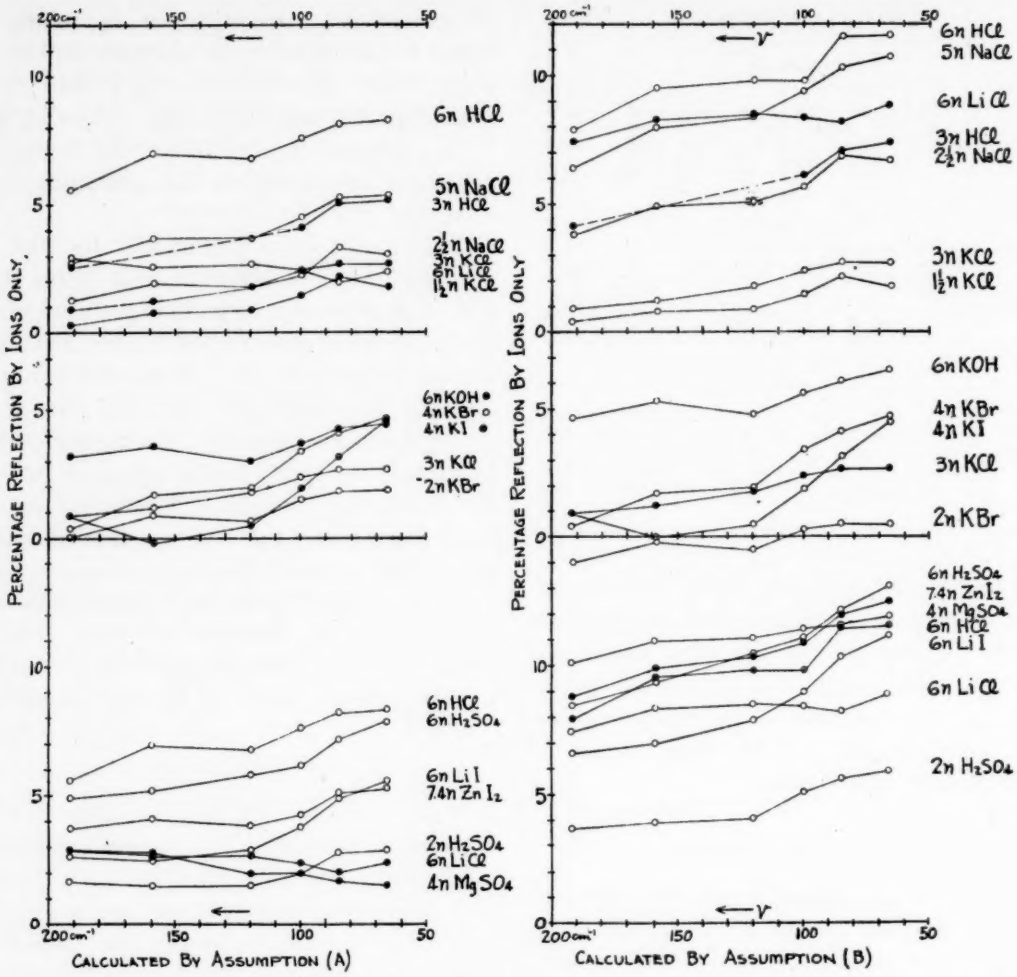

FIG. 4. Absorption due to ions only in various electrolytes as calculated by subtracting the absorption due to water molecules from the observed absorption of the electrolytes.

ions in general increases the intensity of the broad absorption band in water.

2. The reflection due to ions

Figure 5 also shows the reflecting power of water and it is to be observed that the broad absorption band does not influence the reflecting power very much; rather the reflecting power can be almost entirely attributed to an orientation of the permanent dipoles. Thus a study of the reflecting power of the electrolytes should aid in distinguishing the absorption due to ions from the absorption due to the water.

In Fig. 6A is shown the percentage of reflection due to the ions only as obtained by the formula

$$R_{\text{ions}} = R_{\text{mes.}} - (CR)_{H_2O}, \qquad (19)$$

which corresponds to the *assumption* (*A*) underlying the data in Fig. 4A.

In Fig. 6B is shown the percentage of reflection due to the ions only as obtained by the formula

$$R_{\text{ions}} = R_{\text{mes.}} - (CR)_{H_2O}/\eta_{\text{solution}}, \qquad (20)$$

assumption (*B*), which takes into account the findings of Rubens that the reflecting power depends on viscosity. Fig. 6B therefore corresponds to Fig. 4B.

Figures 6A and 6B show that the reflecting power due to ions is much more in harmony with the assumptions underlying the theoretical curve in Fig. 1 than was in general obtained from absorption measurements. This we interpret as additional evidence that in general the

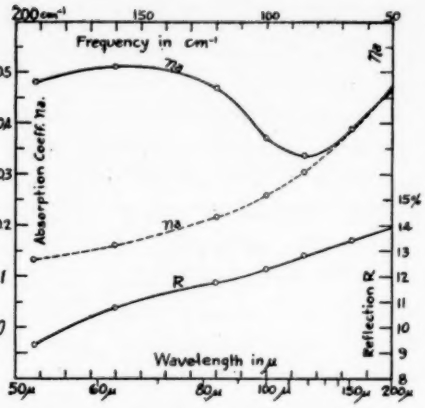

FIG. 5. Reflecting and absorbing power of water.

presence of ions increases the intensity of the broad absorption band in water.

3. Electrical conductivity and ionic radius

In Table IV are given the values for the equivalent electrical conductance as calculated from formula (11). The calculations were made for $\lambda = 117\mu$ and 152μ so as to avoid as much as possible the influence of the water absorption band. A comparison with the conductivities observed for static field in Table III shows our values to be in general too small, especially when we consider that formula (11) assumes $\nu \ll \nu_0$; for $\nu = \nu_0$ the electrical conductivity should be twice as great. This can also be expressed by saying the ionic radii measured by infrared absorption are smaller than the accepted values. In Table IV is shown the average radius of the two types of ions in each electrolyte as calculated from formula (10); taking into account the effect of the inertia of the ions would make the ion radii in Table IV even smaller.

4. Resonance frequency of ions in an electrolyte

It is conceivable that the ions in an electrolyte are bound in a potential field so that an excessive absorption occurs for electromagnetic waves near

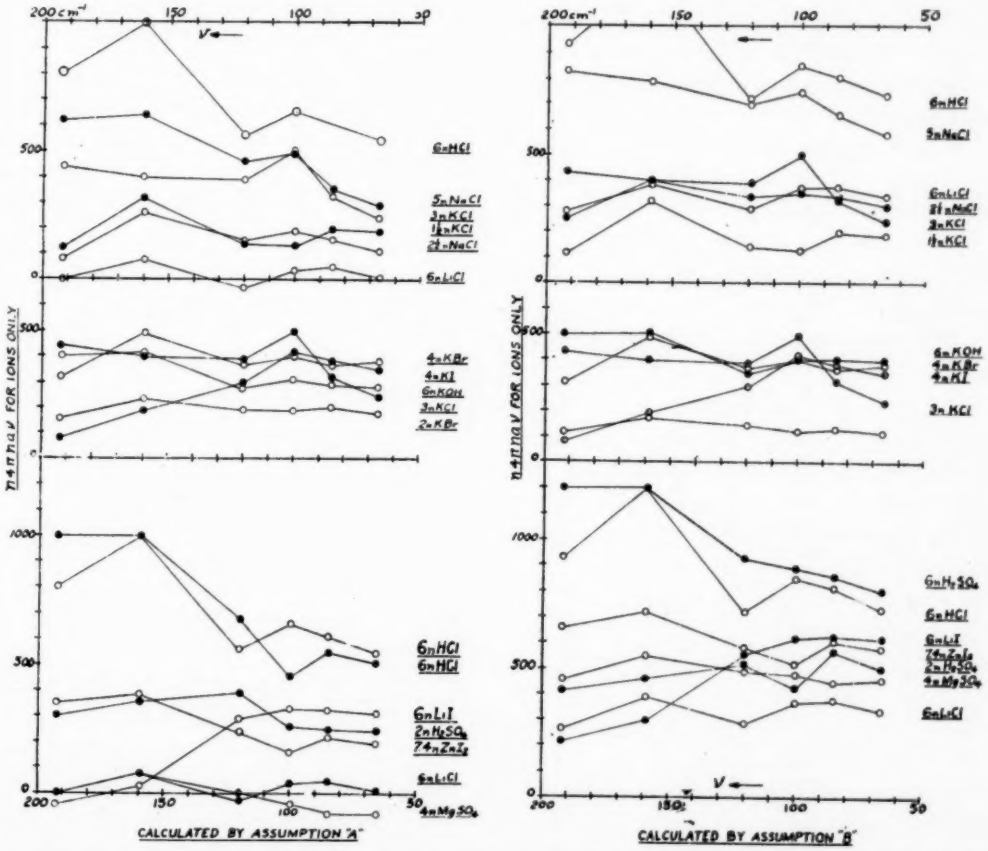

FIG. 6. Reflecting power of ions only as a function of wave-length. Calculated by subtracting the reflecting power of water from the measured reflecting power of various electrolytes.

the resonance frequency. A resonance phenomenon was not taken into consideration in the simple theory we gave and this might explain the rather high values obtained for the electrical conductivity and the apparently small ion radii. The difficulty in accounting for the influence of the water molecules weakens the evidence that our data on conductivity and ion radius show an effect of resonance; but other data strengthens the hypothesis that resonance might occur and occurs in the spectral region we investigated.

There are several independent types of analysis that indicate the molecules in a liquid are bound in a quasicrystalline structure due to intermolecular fields. In the case of water, the two broad bands around 20μ and 60μ can be attributed to an oscillation of the hydrogen atoms[6] (this is in addition to the three fundamental frequencies of the water molecule found in the near infrared). The fact that salts dissolve in water also indicates that the ions in an electrolyte are subjected to strong electric fields. Assuming the field to be the same on an electrolytic ion as on the atoms in water this would give a resonance frequency for

$$\lambda_{\text{in }\mu} = 20M^{\frac{1}{3}}, \qquad (21)$$

where M is the atomic weight of the ion considered. This formula therefore predicts an excessive absorption for many ions in the spectral region we investigated; especially considering that in an electrolyte, any effect due to resonance if it occurs would probably cover a considerably broader spectral region than is observed for ions in crystals. Let us recall too that the ions we studied when in the crystal state have their resonance frequencies in or near the spectral region investigated here. To really answer the question of resonance it is of course necessary to consider analytically a model and take into account that the type (such as neon or argon type) and the radius of an ion would influence the field; however, as a first approximation, it can be assumed that the resonance frequency for heavy ions would in general lie at longer wave-lengths than for light ions. Our data support this assumption, especially for iodine ions.

5. Spectral properties of H^+ and OH^-

Special considerations deserve attention for ions of H^+ and OH^- (and possibly SO_4^{--}) because of permanent dipoles. It has been rather conclusively established that H^+ does not exist alone in an electrolyte but forms an ion of H_3O^+.[7]

[6] C. H. Cartwright, Phys. Rev. **49**, 470 (1936).

[7] M. Kolthoff, Rec. Chem. des Pays-Bas **49**, 401 (1930)

TABLE III. *Electrolytes.*

Electrolyte	Equiv. Normality	cc H_2O per 100 cc Solution	Vol. Conc.	Weight Conc.	Molar Conc.	Viscosity	Spec. Elec. Cond.	Equiv. Elec. Cond.	Equiv. Elec. Cond. for Infinite Dil.
			%	%	%				
HCl	6	87.9	14	19.8	10.9	0.014	0.77	128	379
"	3	94.1	7	10.4	5.4	0.012	0.64	215	
LiCl	6	89.5	12.1	22.0	10.8	0.022	0.17	28	99
"	3	94.0	6.1	11.7	5.4	0.018	0.13	45	
NaCl	5	89.3	13.1	24.6	9.2	0.018	0.21	43	109
"	2.5	95.0	6.6	13.2	4.5	0.014	0.15	60	
KCl	3	90.7	11.1	19.8	5.6	0.010	0.27	88	130
"	1.5	95.5	5.5	10.5	2.8	0.010	0.14	93	
KBr	4	84.9	17.2	35.9	7.8	0.010	0.34	85	132
"	2	92.6	8.7	20.4	3.8	0.009	0.19	95	
LiI	6	78.0	20.3	50.6	12.2	0.022	0.22	37	96
"	3	89.0	10.0	31.0	5.7	0.016	0.16	52	
KI	4	80.3	21.2	45.0	8.3	0.010	0.35	88	131
"	2	90.4	10.6	26.9	3.8	0.009	0.20	100	
ZnI_2	14.7	49.0	50	83	35	——	0.06	4	——
"	7.4	75.0	25	61	15	0.036	0.05	7	
$MgSO_4$	4	97.6	8.4	19.8	6.9	0.048	0.05	12	110
"	2	99.2	4.3	10.8	3.5	0.020	0.04	21	
KOH	6	92.0	15.1	26.8	10.5	0.012	0.56	90	236
"	3	96.9	7.8	14.7	5.3	0.011	0.43	142	
H_2SO_4	2	96.4	5.3	9.3	1.8	0.013	0.36	183	
"	6	88.4	15.4	25.0	6.7	0.018	0.72	120	383
"	12	75.0	30.0	44.0	12.6	0.03	0.63	52	

Hueckel and Fowler have given two interpretations for the anomalously large electrical conductivity of H^+ and OH^- but both agree on proton jumps accompanying the migration of these ions. Recently Wannier[8] has given a quantum-mechanical interpretation for the proton jumps which is based essentially on the Hueckel theory which takes into account a Debye dipole orientation of these ions.

It is questionable that proton jumps would influence the infrared properties of electrolytes but the dipole orientation of an ion should produce a general absorption such that

$$4\pi n a \nu = \text{a constant depending on the dipole moment,} \quad (22)$$

in excess to the absorption of a simple ion.

Our data on KOH indicate a general absorption in agreement with formula (22) but show no particularly large absorption; however, our data on ions of H^+ show evidence of an excess absorption and reflection. Following the theory of dipole absorption for ions of H^+ or more accurately H_3O^+, the effect of dipoles of H_2O and H_3O^+ should be treated separately. Since the formation of H_3O^+ ions results in a diminution in the number of H_2O molecules, an excess absorption over that of simple ions would mean that the electric moment of H_3O^+ is greater than of H_2O.

6. Hydration of ions

For static fields, as shown in Table III, the electrical conductivities of Mg^{++} and Li^+ ions are relatively small and this can be interpreted as evidence that these ions are hydrated or if we assume that all ions are hydrated then more hydrated than is usual for an ion. The fact that electrolytes containing Mg and Li ions are abnormally viscous is also most easily explained by assuming there are strong binding forces between these ions and surrounding water molecules.

The theory we have given does not take into account any direct interaction between the water molecules and ions such as might be the case if hydration occurs. Let us recall that the distinction between assumptions (*A*) and (*B*) is that the latter assumes a change in viscosity due to the presence of ions changes the degree to which the water dipoles are oriented by an electromagnetic field. If the properties of the ions and the water molecules are to a first approximation additive, then we might expect hydrated ions to reflect and absorb less than simple ions and have relatively large ionic radii. Our data in Table IV as calculated according to assumption (*A*) rather indicate that these ions are hydrated but when calculated according to assumption (*B*) they do not.

Table IV.

Electrolyte	Equivalent Normality	Equivalent Electrical Conductance, Λ 0.001 Nor. (*A*)	Equivalent Electrical Conductance, Λ 0.001 Nor. (*B*)	Equivalent Reflecting Power, R 0.001 Nor. (*A*)	Equivalent Reflecting Power, R 0.001 Nor. (*B*)	Average Ion Radius $\times 10^8$ cm (*A*)	Average Ion Radius $\times 10^8$ cm (*B*)
HCl	6	250	330	130	190	0.4	0.3
	3	270	400	180	250	0.5	0.3
LiCl	6	15	170	40	140	4	0.6
NaCl	5	160	300	110	210	0.5	0.3
	2.5	120	320	120	260	0.7	0.3
KCl	3	230	230	90	90	0.4	0.4
	1.5	120	320	120	110	0.5	0.5
KBr	4	250	250	120	110	0.7	0.7
	2	250	150	100	20	0.7	1.0
LiI	6	130	270	90	180	0.5	0.3
KI	4	250	250	110	150	0.6	0.6
ZnI_2	7.4	70	200	70	170	0.6	0.2
$MgSO_4$	4	−50	300	40	300	large	0.1
KOH	6	130	180	70	110	1.0	0.8
	3	100	170	80	120	1.5	1.0
H_2SO_4	2	300	650	150	300	0.4	0.2
	6	220	420	130	220	0.4	0.2

We shall leave the question of hydration for with it arises again the question of ionic resonance as well as the influence on the absorption by the water molecules. Without an analytical model it is difficult to estimate the influence hydration would have on the infrared spectral properties of electrolytes for it depends on the potential functions. The effect might not be very great in the spectral region we investigated. Previous observations on effects attributed to hydration, it should be considered, are for relatively slow motions. Thus liquid water displays spectroscopically two distinct aspects, one pertaining to its crystalline properties in the region of $\lambda = 20\mu$ and $\lambda = 60\mu$ and one pertaining to its dense-gaseous properties which are especially pronounced in the spectral region around $\lambda = 1$ cm.

It seems a criterion for deciding between assumptions (*A*) and (*B*) and whether it is permissible to neglect hydration or other interactions between the ions and water molecules

[8] G. Wannier, Ann. d. Physik **24**, 545 and 569 (1935).

would be to consider the effect of ionic concentration. Unfortunately the data in Table IV do not give a unique answer; but, considering the difficulties in making absolute measurements in this region of the spectrum and the possibility of accumulative errors in calculating, the data in general justify the assumption that the properties of the ions and water molecules are additive.

7. The validity of Stokes' law of friction

Calculating the motion of ions in the electrolytes due to the intensity of radiation of the infrared frequencies we used shows that the displacement of the ions is small compared with 10^{-8} cm. Therefore it is not altogether justified to apply Stokes' law of friction, which was derived for macroscopic processes, to the microscopic phenomenon we investigated.

We introduced Stokes' law as a means of determining the ion radii and possibly it is not surprising that our values are somewhat too small. However, it is to be observed that Stokes' law at least gives the right order of magnitude for the ion radii; or stated otherwise, the calculated frictional forces acting on the ions are in fair agreement with Stokes' law.

The electrical conductivity of ions we obtained without taking account of their radii was greater than is observed for static fields. This might indicate that Stokes' law can be applied to both static and very high frequency fields for calculating ion radii but the effective radii depend on frequency. In view of the difficulties already mentioned in assigning a value to the absorption due only to the ions, it seems possible that we have overestimated their absorption and hence obtained in general too high values for the electrical conductivities. However, if such were the case it would mean that Stokes' law of friction can be used very well for even microscopic movements of ions in electrolytes.

Acknowledgments

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The Absorption Spectrum of Diacetylene in the Near Ultraviolet. II

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The absorption spectrum of diacetylene has been reinvestigated with an instrument of higher dispersion. The bands in the region λλ2970–2650A are sharp and narrow, and very closely spaced. Two progressions with a frequency difference ~690 cm^{-1} have been found. Those below λ2650A are very diffuse, but with a comparatively simpler gross structure. Ten progressions all with a frequency difference ~2100 cm^{-1} have been found. Through a brief and qualitative discussion of the normal vibrations and symmetry properties of the molecule, the frequency differences ~2100 cm^{-1} and ~1900 cm^{-1} are respectively ascribed as the totally symmetrical $\nu'_{c\equiv c}(s)$ and unsymmetrical $\nu'_{c\equiv c}(a)$ longitudinal frequencies in the excited state. The frequency ~635 cm^{-1} is assigned as one of the fundamental frequencies in the normal state, since bands with this frequency difference were relatively intensified at higher temperatures.

IN a recent communication[1] (which will hereafter be designated as I), the results of our previous investigation of the absorption spectrum of diacetylene were reported. The spectrum was then taken with a small Hilger quartz spectrograph. The gross structure of the spectrum

[1] Sho-Chow Woo and T. C. Chu, J. Chem. Phys. **3**, 541 (1935).

seemed to point to the necessity of a more detailed study with a more powerful instrument. Experiments have thus been carried out with our since then available instrument of higher dispersion.

The experimental arrangement was essentially the same as that used by Woo and Liu.[2] The Bausch and Lomb large quartz spectrograph has a dispersion in the region of interest about ten times greater than the Hilger E31 used in our previous experiments. Absorption tubes of 3 cm, 50 cm and 350 cm long with varying pressures up to 745 mm were used in order to develop the bands as far as possible. Besides the repeated fractionation under reduced pressure, the purity of the gas was further evidenced by being passed through an ammoniacal solution of cuprous chloride and regenerated from the precipitated copper diacetylide with dilute hydrochloric acid. The contamination of the gas with acetylene, which may not be removed by the above treatment, was excluded by the absence of the well-known spectrum of acetylene. On account of the easy polymerization of the diacetylene gas, absorption at higher temperature (~250°C) has been carried out only at very low pressures (<1–2.5 mm) of the absorbing gas. Microphotometer tracings for a number of plates were made through the kidness of Dr. Ny Tsi-Zé and Mr. Chyan San-Chyang, to whom the authors wish to express their sincere gratitude.

The results of the present investigation agree well with those of I. However, since we used greater dispersion and wider variation of the experimental conditions in the present investigation, the spectrum was much better developed than before. Many of the previously overlapping bands have been resolved to some extent and numerous new ones have come into appearance. Table I gives the wave-lengths and wave numbers of the bands measured with their relative intensities visually estimated. Because of the strong pressure broadening of the low pressure bands and a comparatively finer adjustment of the pressure in the present investigation, the measured wave-lengths of these bands differ somewhat from those of the corresponding ones given before. The spectrum extends from λ2970A down to the ultraviolet limit of the spectrograph with increasing intensity. The complete spectrum consists of two parts of apparently very different gross structure. They constitute probably two different electronic systems which will be treated separately.

[2] Sho-Chow Woo and Ta-Kong Liu, J. Chem. Phys. **5**, 161 (1937).

High Pressure Bands

The bands on the longer wave-length side began to appear only at comparatively high pressures. These bands are so sharp and narrow that they appear as individual lines, the average separation between almost any two of them being about 4–5 cm^{-1}. The "lines" are so numerous and closely spaced that the spectrum appears apparently very open and without any prominent head. Very little regularity could be found from the gross structure. Many weak bands on the red side of some stronger ones have been found with frequency differences ~230, ~460, ~488 and ~644 cm^{-1}. These could be ascribed as due to transitions from excited vibrational levels in the ground state. However, since the "lines" are so closely spaced that any scheme of analysis could fit in with some satisfaction, it is not advisable at present to draw any conclusion about these possibilities, unless an unambiguously consistent analysis could be provided. Two progressions of stronger bands with reasonable intensity distribution can, however, be assigned with certainty. These are listed in Table II. Each pair of the bands may be considered as doublets with a separation of about 50 cm^{-1}. The complexity of the gross structure of this system of bands is possibly due to the transformation of the diacetylene molecule into the bent form in the excited state by the electronic excitation. This changes the symmetry properties of the molecule and modifies the selection rules applicable to symmetrical collinear molecules. Besides, the molecule in the excited state will then possess three moments of inertia, one of which is probably much smaller. This will also cause the spectrum to assume an open structure.

Low Pressure Bands

The bands below λ2650A become increasingly diffuse. Those below 2500A are specially so, so that no resolution could be effected by varying

TABLE I. *The diacetylene bands in the near ultraviolet.*

λ(A)	ν(CM⁻¹)	I	λ(A)	ν(CM⁻¹)	I	λ(A)	ν(CM⁻¹)	I	λ(A)	ν(CM⁻¹)	I	λ(A)	ν(CM⁻¹)	I
2970.0	33660.2	00	2826.5	35369.1	00	2782.6	35927.0	0	2736.8	36528.2	0	2688.1	37190.0	1
2958.4	33792.2	00	2826.3	35371.6	00	2782.34	35930.4	2	2736.4	36533.6	0	2687.4	37199.7	1
2917.70	34263.6	1	2826.0	35375.3	00	2781.33	35943.4	0	2735.5	36545.6	0	2686.4	37213.5	1
2917.02	34271.6	1	2825.8	35377.8	00	2781.0	35947.7	00	2735.16	36550.1	1	2685.8	37221.8	0
2916.96	34272.3	0	2825.5	35381.6	00	2780.7	35951.6	00	2734.36	36560.8	2	2685.2	37230.1	1
2913.30	34315.3	0	2825.3	35384.1	00	2780.27	35957.1	3	2733.84	36567.8	1	2684.5	37239.8	0
2912.40	34325.9	0	2825.1	35386.6	00	2779.45	35967.7	0	2733.2	36576.3	1	2684.2	37244.0	0
2911.75	34332.6	1	2824.9	35389.1	00	2779.1	35972.3	00	2732.18	36590.0	1	2683.3	37256.5	0
2911.45	34337.1	1	2822.0	35425.5	00	2778.69	35977.6	00	2731.86	36594.3	1	2682.3	37270.4	0
2909.7	34357.8	0	2821.7	35429.2	00	2778.47	35980.5	00	2731.3	36601.8	0	2680.4	37296.8	3
2908.95	34366.6	0	2820.82	35440.3	1	2777.7	35990.4	00	2730.8	36608.5	0	2680.1	37301.0	1
2908.65	34370.2	0	2820.35	35446.2	1	2776.14	36010.6	0	2730.4	36613.9	1	2679.85	37304.5	3
2908.3	34374.3	0	2820.0	35450.6	0	2775.28	36021.8	2	2730.0	36619.2	1	2679.4	37310.7	1
2907.65	34382.0	1	2819.50	35456.9	3	2774.72	36029.1	0	2729.2	36629.9	2	2679.09	37315.0	3
2907.3	34386.1	0	2819.2	35460.6	00	2774.26	36035.0	0	2728.7	36636.7	1	2678.6	37321.9	2
2906.3	34398.0	0	2818.7	35466.9	0	2773.66	36042.8	0	2727.5	36652.8	1	2678.3	37326.0	2
2904.95	34413.9	0	2818.4	35470.7	0	2773.3	36047.5	00	2726.8	36662.2	1	2677.9	37331.6	2
2900.32	34468.9	1	2818.1	35474.5	0	2773.08	36050.4	3	2726.5	36666.2	2	2675.5	37365.1	2
2899.64	34477 0	0	2817.7	35479.5	0	2771.8	36067.0	00	2726.2	36670.3	1	2675.0	37372.1	2
2898.8	34487.0	0	2817.45	35482.6	1	2771.42	36071.9	2	2725.72	36676.7	3	2674.7	37376.3	2
2897.7	34500.0	0	2816.4	35495.9	0	2771.04	36076.9	0	2725.17	36684.1	3	2674.4	37380.5	2
2897.4	34503.6	0	2815.8	35503.5	00	2770.47	36084.3	1	2724.84	36688.5	0	2673.9	37387.5	3
2896.53	34514.0	1	2815.4	35508.5	00	2769.88	36092.0	1	2724.6	36690.8	0	2673.2	37397.3	2
2895.5	34526.3	0	2815.00	35513.5	2	2769.36	36098.8	2	2724.3	36695.8	1	2672.3	37409.8	2
2880.9	34701.2	0	2814.52	35519.6	1	2768.86	36105.3	0	2723.99	36700.0	1	2672.0	37414.0	2
2878.3	34732.6	0	2814.23	35523.3	2	2768.3	36112.6	00	2723.4	36708.0	0	2671.6	37419.6	4
2875.5	34766.4	0	2813.8	35528.7	00	2768.02	36116.3	1	2722.7	36717.4	1	2671.3	37423.8	4
2874.1	34783.3	0	2813.5	35532.5	00	2767.6	36121.7	00	2722.08	36725.8	3	2670.9	37429.5	4
2871.2	34818.4	0	2813.33	35534.6	3	2766.0	36142.6	00	2721.5	36733.6	1	2670.3	37437.9	2
2870.7	34824.5	0	2813.0	35538.8	0	2765.36	36151.0	1	2721.09	36739.1	3	2669.6	37447.7	3
2866.6	34874.3	0	2812.71	35542.5	2	2764.63	36160.6	0	2720.8	36743.0	1	2668.9	37457.5	1
2865.26	34890.6	2	2812.5	35545.1	0	2763.60	36174.0	0	2720.51	36746.9	2	2668.3	37465.9	1
2865.0	34893.8	0	2812.03	35551.0	1	2762.46	36188.9	0	2720.09	36752.6	2	2667.3	37480.0	3
2864.73	34897.1	0	2811.4	35559.0	0	2761.99	36195.1	1	2719.85	36755.8	1	2666.7	37488.4	3
2864.37	34901.5	0	2810.63	35568.8	4	2761.61	36200.1	0	2719.45	36761.3	2	2666.0	37498.2	3
2864.03	34905.6	2	2810.25	35573.6	0	2760.95	36208.7	0	2718.63	36772.4	1	2665.5	37505.3	2
2863.74	34909.2	0	2810.03	35576.4	1	2760.34	36217.3	0	2718.5	36774.1	0	2664.6	37517.9	1
2863.45	34912.7	3	2809.80	35579.3	5	2759.94	36222.0	0	2717.93	36781.8	4	2664.2	37523.6	1
2862.5	34924.3	0	2809.51	35582.9	1	2759.60	36226.5	0	2717.04	36793.9	3	2663.7	37530.6	1
2861.85	34932.2	4	2809.29	35585.7	3	2758.91	36235.5	2	2716.33	36803.5	2	2663.1	37539.1	1
2860.84	34944.7	1	2808.99	35589.5	2	2758.36	36242.7	3	2712.1	36860.9	0	2661.3	37564.5	1
2859.89	34956.1	1	2808.6	35594.5	00	2757.78	36250.3	2	2711.9	36863.6	0	2660.5	37575.8	2
2859.2	34964.6	0	2808.02	35602.3	0	2757.51	36252.9	3	2709.7	36893.5	1	2660.1	37581.4	2
2858.64	34971.4	1	2807.41	35609.6	4	2757.12	36259.0	1	2709.3	36899.0	1	2659.4	37591.3	3
2858.1	34978.0	0	2806.71	35618.4	0	2756.87	36262.3	1	2707.4	36924.9	2	2659.0	37597.0	3
2857.04	34991.0	2	2806.50	35621.1	3	2756.58	36266.1	4	2707.1	36929.0	1	2658.7	37601.2	3
2856.7	34995.2	00	2806.25	35624.3	5	2756.28	36270.1	1	2706.89	36931.8	3	2656.9	37626.7	1
2856.38	34999.2	0	2805.9	35628.7	00	2756.06	36273.0	1	2706.53	36936.6	1	2656.1	37638.0	2
2856.1	35002.5	00	2805.7	35631.3	00	2755.74	36277.2	5	2706.1	36942.6	3	2655.5	37646.5	2
2855.90	35005.0	2	2805.51	35633.7	3	2755.50	36280.4	0	2705.4	36952.2	1	2654.9	37655.0	2
2855.67	35007.8	2	2803.92	35653.9	2	2755.27	36283.4	1	2704.97	36958.0	2	2654.5	37660.9	4
2855.2	35013.6	00	2803.49	35659.3	3	2755.03	36286.5	0	2704.51	36964.3	3	2654.2	37664.9	4
2854.9	35017.2	0	2802.98	35665.7	2	2754.67	36291.3	0	2704.2	36968.6	2	2654.0	37667.8	4
2854.7	35019.7	0	2802.06	35677.5	1	2754.25	36296.8	0	2703.85	36973.4	7	2653.5	37674.9	3
2854.25	35025.2	2	2801.60	35683.4	0	2753.78	36303.0	0	2703.3	36980.8	1	2652.9	37683.4	3
2853.63	35032.8	1	2800.93	35691.9	1	2753.15	36311.3	1	2703.0	36985.0	0	2652.4	37690.5	3
2853.34	35036.4	4	2800.23	35700.9	1	2752.92	36314.4	1	2702.7	36989.1	2	2651.9	37697.6	4
2852.84	35042.5	2	2799.41	35711.3	3	2752.70	36317.3	3	2702.45	36992.5	2	2651.7	37700.4	4
2852.20	35050.4	0	2799.2	35714.0	0	2752.30	36322.5	4	2702.18	36996.2	4	2651.4	37704.7	4
2851.54	35058.5	3	2798.92	35717.6	3	2751.90	36327.8	1	2701.8	37001.4	0	2651.1	37709.0	4
2851.1	35063.9	0	2798.67	35720.7	1	2751.64	36331.3	0	2701.6	37004.1	0	2650.8	37713.2	5
2850.8	35067.6	0	2798.3	35725.5	1	2751.35	36335.1	0	2701.3	37008.3	2	2650.5	37717.5	2
2850.5	35071.3	00	2798.10	35728.0	1	2751.15	36337.7	0	2701.0	37012.4	2	2650.25	37721.1	7
2850.25	35074.3	3	2797.9	35730.6	0	2750.60	36345.0	0	2700.5	37019.2	2	2649.8	37727.5	4
2849.7	35081.1	0	2796.8	35744.6	0	2750.30	36348.4	1	2700.2	37023.3	2	2649.5	37731.7	2
2849.1	35088.5	0	2795.60	35760.0	1	2749.85	36354.9	1	2699.93	37027.0	3	2649.2	37736.0	2
2848.3	35098.4	0	2794.96	35768.2	1	2749.67	36357.3	1	2699.5	37032.9	2	2648.1	37751.7	1
2847.7	35105.8	0	2794.6	35772.8	0	2749.34	36361.6	1	2698.7	37043.9	1	2647.7	37757.6	2
2847.0	35114.4	0	2794.25	35777.3	3	2749.04	36365.6	1	2698.2	37050.8	2	2647.4	37761.7	1
2845.4	35134.1	0	2793.7	35784.3	0	2748.75	36369.4	0	2697.8	37056.3	1	2647.0	37767.4	2
2844.8	35141.5	0	2793.0	35793.3	00	2748.52	36372.5	0	2698.2	37050.8	2	2646.3	37777.4	1
2844.3	35147.7	0	2792.4	35801.0	00	2748.05	36378.7	2	2697.8	37056.3	1	2645.7	37785.9	2
2844.08	35150.5*	1	2791.8	35808.6	00	2747.73	36382.9	3	2697.3	37063.1	1	2645.2	37793.1	1
2843.0	35163.8	00	2791.3	35815.1	00	2747.36	36387.8	3	2696.9	37068.6	1	2644.3	37605.9	2
2842.7	35167.5	0	2791.09	35817.8	1	2747.06	36391.8	1	2696.6	37072.8	2	2644.0	37810.2	2
2842.3	35172.5	0	2790.5	35825.3	00	2746.71	36396.5	3	2696.2	37078.3	1	2643.6	37816.0	2
2841.76	35179.1	2	2790.1	35830.5	00	2746.45	36399.9	3	2695.9	37082.4	2	2643.2	37821.7	1
2841.23	35185.7	0	2789.71	35835.5	1	2746.20	36403.2	0	2695.4	37089.3	2	2642.8	37827.4	1
2840.72	35192.0	0	2789.1	35843.3	00	2745.98	36406.1	3	2695.0	37094.8	3	2642.0	37838.8	1
2840.1	35199.7	0	2788.7	35848.5	00	2745.44	36413.3	1	2694.7	37098.9	0	2641.0	37853.2	2
2839.98	35201.2	1	2788.23	35854.5	2	2745.26	36415.7	0	2694.5	37101.6	2	2640.5	37860.3	2
2839.5	35207.1	00	2787.8	35860.0	0	2744.99	36419.3	1	2694.2	37105.8	0	2639.9	37869.0	4
2837.5	35232.0	0	2787.4	35865.2	00	2744.2	36429.7	0	2693.8	37111.3	2	2639.3	37877.6	4
2837.04	35237.7	1	2786.95	35871.0	00	2743.93	36433.3	1	2693.5	37115.4	0	2638.3	37891.9	3
2836.5	35244.4	0	2786.47	35877.1	1	2742.8	36448.3	0	2693.3	37118.2	3	2637.6	37902.0	2
2836.0	35250.6	0	2785.78	35886.0	0	2742.58	36451.3	3	2692.0	37136.1	0	2636.1	37923.5	2
2833.44	35282.4	0	2784.90	35897.4	1	2742.3	36455.0	0	2691.6	37141.6	2	2635.7	37929.3	1
2832.8	35290.4	00	2784.2	35906.4	0	2741.9	36460.3	0	2690.8	37152.7	2	2635.2	37936.5	3
2381.1	35311.6	00	2783.90	35910.3	0	2740.8	36474.9	0	2690.1	37162.3	2	2635.0	37939.4	1
2829.8	35327.8	0	2783.41	35916.6	0	2739.34	36494.5	3	2689.5	37170.6	2	2634.5	37946.6	2
2828.9	35339.1	00	2783.16	35919.8	2	2738.78	36501.8	1	2688.9	37178.9	2	2633.8	37956.7	3
2828.4	35345.3	00	2782.8	35924.5	0	2737.40	36520.2	1	2688.7	37181.7	1	2633.2	37965.3	2

TABLE I.—*Continued.*

λ(A)	ν(CM⁻¹)	I	λ(A)	ν(CM⁻¹)	I	λ(A)	ν(CM⁻¹)	I	λ(A)	ν(CM⁻¹)	I	λ(A)	ν(CM⁻¹)	I
2632.6	37974.0	2	2620.6	38147.8	2	2616.3	38210.5	2	2607.9	38333.6	4	2601.7	38424.9	2
2632.0	37982.6	3	2620.3	38152.2	2	2615.8	38217.8	2	2607.6	38338.0	4	2601.3	38430.8	3
2631.8	37985.5	3	2620.0	38156.6	2	2611.5	38280.8	1	2606.9	38348.3	3	2600.9	38436.8	5
2631.5	37989.8	3	2619.5	38163.8	4	2610.9	38289.5	2	2606.3	38357.1	3	2600.1	38448.6	5
2631.2	37994.2	2	2619.2	38168.2	2	2610.6	38293.9	2	2606.1	38360.1	3	2599.7	38454.5	2
2630.7	38001.4	1	2618.9	38172.6	6	2609.9	38304.2	2	2605.7	38366.0	1	2597.5	38487.1	2
2626.5	38062.1	1	2618.5	38178.4	3	2609.2	38314.5	3	2604.5	38383.6	1	2596.8	38497.4	2
2623.6	38104.2	1	2618.0	38185.7	6	2608.9	38318.9	3	2603.3	38401.3	1	2595.7	38513.7	2
2622.2	38124.6	1	2617.5	38193.0	2	2608.5	38324.8	5	2603.1	38404.3	1	2594.7	38528.6	2
2621.5	38134.7	2	2617.2	38197.4	3	2608.2	38329.2	5	2602.7	38410.2	3	2593.3	38549.4	1

M	λ(A)	ν(CM⁻¹)	I	D	M	λ(A)	ν(CM⁻¹)	I	D	M	λ(A)	ν(CM⁻¹)	I	D	M	λ(A)	ν(CM⁻¹)	I	D
C	2588.3	38624	3			2460.6	40628	2			2377.8	42043				2257.8	44277	1	
C	2585.2	38670	1			2459.7	40643			MI	2376.9	42059	5	F		2256.5	44303		
C	2582.4	38712	1		C	2455.6	40711	1			2374.5	42101				2254.2	44348	2	G'
C	2579.2	38760	1			2451.8	40774	1			2365.8	42256	3	G		2252.2	44387		
C	2575.8	38811	2			2450.5	40796				2364.2	42285				2247.4	44482	2	H'
	2565.7	38964	1			2448.2	40834	1			2361.6	42331	4	H		2246.4	44502		
	2565.2	38972	2			2446.0	40871				2358.6	42385			C	2243.8	44553	1	
	2563.8	38993	3			2440.4	40965				2353.6	42475	3			2240.1	44627	1	
	2563.3	39001	3		C	2439.6	40978	2	J		2351.1	42520				2239.2	44645		
	2562.8	39008	3			2439.0	40988				2349.0	42558				2237.7	44675		
	2560.6	39042	4			2433.8	41076			MI	2346.5	42605	5	I'	C	2236.8	44693	4	I''
	2560.2	39048	5	A°	C	2433.0	41089	10			2345.8	42617				2235.8	44713		
	2559.8	39054	5			2432.3	41100				2340.6	42711	1		C	2232.6	44777	1	
	2559.4	39060	4		L	2431.3	41118	4	A		2337.0	42777			C	2214.9	45135	1	J''
	2557.8	39084	3		L	2430.8	41125	4			2332.0	42869	1			2209.6	45243		
	2556.8	39100				2430.6	41130				2330.8	42891			MI	2205.5	45327	6	A''
	2555.8	39115	3		C	2430.3	41135	5			2328.0	42942	2			2204.6	45346		
	2555.4	39121				2429.9	41141				2325.6	42986				2197.9	45484	3	B''
C	2554.6	39133	2			2422.9	41260				2322.7	43040				2196.1	45521		
C	2554.0	39143	2		C	2422.4	41269	7	B	C	2321.3	43066	2	J'		2189.9	45650	3	C''
	2541.8	39330				2421.8	41279				2319.7	43096				2188.7	45675		
C	2541.5	39335	2			2419.5	41318	1			2314.7	43189			C	2185.3	45746	3	D''
	2541.3	39338				2418.5	41335			C	2313.8	43207	9		C	2181.4	45828	2	
	2534.0	39451	2			2413.5	41421	1			2313.1	43219			C	2178.9	45880	3	E''
	2532.8	39470				2412.1	41445			L	2312.6	43229	4	A'	C	2175.1	45960	2	
	2529.1	39528	3			2408.6	41505				2312.1	43239				2162.6	46226	3	F''
	2525.0	39592			C	2408.2	41512	7	C	C	2311.9	43242	5			2160.4	46273		
	2515.7	39738	3			2407.8	41519				2311.7	43245			C	2155.3	46383	1	
	2512.5	39789				2404.8	41571				2304.9	43373	5	B'	C	2151.2	46471	1	G''
	2509.7	39833	3		C	2404.2	41581	7	D		2302.8	43411			C	2144.3	46621	1	H''
	2505.7	39897				2403.6	41592				2294.7	43565	5	C'	C	2138.2	46759	1	I'''
	2502.9	39942	3			2395.7	41730				2292.6	43605			C	2118.1	47197	1	J'''
	2498.5	40012			C	2395.0	41740	8			2289.3	43668	5	D'		2111.1	47354		
	2486.8	40200				2394.5	41750		E		2288.3	43687			MI	2109.2	47396	3	A''''
C	2485.9	40215	4			2394.1	41756				2285.1	43748				2108.8	47405		
	2485.3	40224			C	2393.8	41761	5		MI	2282.9	43790	6	E'		2101.3	47574	1	B'''
	2477.8	40346	3			2393.5	41766				2281.6	43815				2100.0	47604		
	2476.5	40367				2390.5	41820	2			2277.2	43900				2097.0	47672	1	C''''
	2471.5	40449				2389.2	41842			C	2276.3	43917	3			2095.1	47715		
L	2469.3	40486	5			2386.8	41884	1			2275.7	43929			C	2090.8	47813	1	D''''
L	2468.8	40494	6	I		2385.1	41914			C	2272.7	43987	1		C	2084.8	47951	1	E'''
L	2468.3	40502	6			2382.3	41963	1		C	2269.6	44047	1			2070.4	48284	1	F''''
	2467.5	40515				2380.8	41990				2264.7	44142	4	F'		2068.5	48329		
	2463.9	40574	1								2262.1	44194							
	2462.2	40602																	

In columns *M*, broader bands are given under brackets. *C* or *MI* specifies the center or the part of maximum intensity of the band measured. *L* = "Line" or very narrow band. In columns *I* and *D* are given their estimated relative intensities and designations.

the experimental conditions such as pressure, plates and slit width. Since it will be seen later that the electronic excitation has taken place at the C≡C bond, it is probable that predissociation must have occurred at the C−C bond. This being the case, the estimated energy of dissociation amounts approximately to 107 kcal./mole.

The gross structure of the low pressure system is comparatively simple and some regularities of the vibrational structure may be observed. The strongest band *A* at 2430A has been resolved to some extent at pressures less than 1 mm with an absorbing path of 50 cm. But further improvement could not be made with further adjustment of the experimental conditions. In Table III are given the progressions found in the low pressure system of bands including those previously reported. All of these progressions have a frequency difference of about 2100 cm^{-1}. The frequency differences between bands of different progressions should usually be assigned as fundamentals or combinations in the excited state. But they are too many here to be all so assigned. Moreover, these differences are far from being approximate constants and vary rather irregularly. Complications might have come in from two possibilities: (1) the resonance between

TABLE II. *Progressions in C_4H_2 "high pressure systems."*

ν(cm^{-1})	I	$\delta\nu$	$\Delta\nu$
24932	4		
			692
35579	5	45	
35624	5		
			698
			699
36277	5	46	
36323	4		
			696
			704
36973	7	54	
37027	3		
			695
			694
37668	4	53	
37721	7		
			692
			689
38360	3	50	
38410	3		
			694
			690
39054	5	46	
39100	3		

nearly coincident levels of fundamentals and harmonics of the different vibrations in the excited state and (2) the interaction between the excited electronic state and the deformation oscillations, if the former be degenerate. Nevertheless, certain plausible assignments may still be made from what we have known about the fundamental frequencies of the molecule in the ground state and the selection rules governing the transitions in an electronic system of a symmetrical collinear molecule.

The fundamental frequencies of the diacetylene molecule in the ground state have been discussed by Timm and Mecke.[3] The assignment of these authors has recently been examined by Wu and Shen[4] with a detailed calculation of the force constants and a critical discussion of the selection rules for infrared and Raman spectra. It is true

[3] B. Timm and R. Mecke, Zeits. f. Physik **94**, 1 (1935).
[4] Ta-You Wu and S. T. Shen, Chinese J. Phys. **2**, 128 (1936).

TABLE III. *Progressions in C_4H_2 "low pressure system."*

ν(CM^{-1})		$\Delta\nu$	ν(CM^{-1})		$\Delta\nu$	ν(CM^{-1})		$\Delta\nu$
A			*B*			*C*		
$A°$	39048							
		2087						
A	41135		B	41279		C	41519	
		2107			2132			2086
A'	43242		B'	43411		C'	43605	
		2085			2110			2070
A''	45327		B''	45521		C''	45675	
		2069			2083			2040
A'''	47396		B'''	47604		C'''	47715	
D			*E*			*F*		
D	41592		E	41761		F	42101	
		2095			2054			2093
D'	43687		E'	43815		F'	44194	
		2059			2065			2079
D''	45746		E''	45880		F''	46273	
		2067			2071			2056
D'''	47813		E'''	47951		F'''	48329	
G			*H*			*I*		
G	42285		H	42385		I	40502	
		2102			2117			2103
G'	44387		H'	44502		I'	42605	
		2084			2119			2088
G''	46471		H''	46621		I''	44693	
								2066
						I'''	46759	
J								
J	40978							
		2088						
J'	43066							
		2069						
J''	45135							
		2062						
J'''	47197							

$A - I = 633$
$A' - I' = 637$
$A'' - I'' = 634$
$A''' - I''' = 637$

TABLE IV. *Deformation force constants.*

MOLECULE	ν(CM^{-1})	$k_1\left(\frac{\text{DYNE CM}}{\text{RADIAN}}\right)$	$k_2\left(\frac{\text{DYNE CM}}{\text{RADIAN}}\right)$	REFERENCE
H−C≡N	δ 709	2.41×10^{-12}	——	6
H−C≡C−H	$\delta(a)$ 730 $\delta(s)$ 605	2.44×10^{-12}	0.92×10^{-12}	5
N≡C−C≡N	$\delta(a)$ 230 $\delta(s)$ 510	2.93×10^{-12}	-0.24×10^{-12}	6
H−C≡C−C≡C−H	$\delta_C(a)$ 231 $\delta_C(s)$ 488 $\delta_{CH}(a)$ 730 $\delta_{CH}(s)$ 720	2.6×10^{-12}(H−C and C≡C) 3.6×10^{-12}(C−C and C≡C)	0.14×10^{-12} 0.15×10^{-12}	4

k_1 = force constant of bending between the neighboring single and triple bonds, *viz.*, $o-o\equiv o$.
k_2 = force constant of interaction between the bendings of two single bonds with a common triple bond, *viz.*, $o-o\equiv o-o$, or of two triple bonds with a common single bond, *viz.*, $o\equiv o-o\equiv o$.

that the assignment of the deformation frequencies of Timm and Mecke is confronted with serious difficulties from the selection rules. It may, however, be interesting to note that the force constants calculated from the values of these authors seem to be comparable with those of other similar molecules (Table IV).[7] We agree with the suggestion of Wu and Shen that a reexamination of the Raman spectrum of diacetylene is necessary to settle this problem. But in the present analysis we are essentially concerned with the longitudinal vibrations for which there seems to be not much difficulty.[8] Regarding the symmetry properties of the diacetylene molecule and the selection rules governing the transitions between the different vibrations, what has been discussed in the spectrum of cyanogen[2] may be essentially applicable here. Thus the frequency difference $\sim$2100 cm^{-1} must be the frequency $\nu'_{c\equiv c}(s)$ of the totally symmetrical vibration in the excited state and the electronic excitation has probably taken place mainly at C≡C bond. The difference $\sim$1900 cm^{-1} ($J-A=1931$, 1893, 1870 cm^{-1}) which only weakly appeared in the spectrum, is probably the frequency of the vibration $\nu'_{c\equiv c}(a)$. The differences between the A and B, and the C and D bands are too small to be ascribed to fundamental frequencies. Whether they may be described as doublets given rise through resonance between nearly coincident levels of fundamentals and harmonics of the different vibrations is uncertain. The only bands which showed appreciably relative intensification at higher temperatures are the I bands. Thus they are considered as due to transitions from the excited vibrational levels with $\nu\sim640$ cm^{-1} (633, 637, 634, 637 cm^{-1}) in the ground state.

In conclusion the authors want to express their sincere thanks to Professor Richard M. Badger for his kindness in reading the manuscript before publication.

[5] W. F. Colby, Phys. Rev. **47**, 388 (1935).
[6] Unpublished results.
[7] It may be admitted that the force constant K_2 plays also a considerable part in affecting the deformation frequencies and the values here obtained vary considerably for different molecules. However, the values of K_1, which is of primary importance here, are of the same order of magnitude for these molecules.
[8] The value 644 cm^{-1} seems to be too small for the frequency $\nu''_{c-c}(s)$ (see reference 4). For the corresponding force constant $k_1(c-c)$ of cyanogen, see reference 2, Table V.

A Method for Deriving Expressions for the First Partial Derivatives of Thermodynamic Functions

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By this direct method, any first partial derivative of the thermodynamic functions may be readily resolved into terms of temperature, pressure, volume, and entropy, and of six basic forms of a mathematical quantity named a vired. These six basic vireds have been expressed in terms of the better known and more easily measurable thermodynamic quantities and therefore may be used in determining any of the first partial derivatives. This method stresses the interrelationship between the partial derivatives and is a distinct departure from Bridgman's method for obtaining expressions for the first derivatives by substitution from a list of 45 arbitrarily defined quantities which have been expressed in simpler terms.

FOR the general use of equations involving partial derivatives of thermodynamic functions, the partial derivatives first need to be resolved into better known or more easily measurable terms. However, the general method for simplification usually involves a good working knowledge of differential calculus and an ingenuity of the sort needed in solving trigonometric identities.

From the ten thermodynamic functions usually selected as fundamental, there are altogether 720 partial derivatives of the form $(\partial x/\partial z)_y$, where x, y, z are any three of the ten functions.

To simplify the determination of this large number of derivatives, P. W. Bridgman[1] sets up 90 quantities of the type $(\partial x)_y$ defined so that the quotient of pairs of them form all the possible first partial derivatives. Thus the partial derivative, $(\partial x/\partial z)_y$, may be denoted as $(\partial x)_y/(\partial z)_y$. By further restricting the relationship of these quantities so that $(\partial x)_y=-(\partial y)_x$, he cuts the number required from 90 to 45. Bridgman has resolved these 45 quantities into terms of the more desirable thermodynamic functions and partial derivatives. From these quantities any of the 720 partial derivatives may be determined by substitution and use of algebra.

A method is here presented based on quantities similar to those devised by Bridgman but redefined in such a manner so as to permit the resolution of the 45 forms into a few, more basic forms. The following ten thermodynamic functions are used:

T, the temperature,
P, the pressure,
V, the volume,
S, the entropy,
dW, the increment[2] of work done by the system,

where $$dW=PdV, \tag{1}$$

dQ, the increment[2] of heat absorbed by the system where $$dQ=TdS, \tag{2}$$

U, the internal energy of the system, where

$$dU=dQ-dW=TdS-PdV, \tag{3}$$

H, the heat content or total heat, defined as

$$H=U+PV, \tag{4}$$

A, the free energy of Helmholtz, defined as

$$A=U-TS, \tag{5}$$

F, the free energy of Gibbs, defined as

$$F=U+PV-TS. \tag{6}$$

Let us set up a quantity dx_y, where x and y are any two of the ten functions, and define it as the product of two partial derivatives, thus:

$$dx_y=-(\partial x/\partial P)_y(\partial y/\partial T)_P.^3 \tag{7}$$

We may designate this form as the *vired*[4] of x with y constant.

[1] P. W. Bridgman, Phys. Rev. **3**, 273 (1914), also *A Condensed Collection of Thermodynamic Formulas* (Harvard University Press, 1925).

[2] Increments of these energy functions are used since the total functions are dependent on the path of change.

[3] Bridgman defines his quantity as $(\partial x)_y=(\partial x/\partial a)_y$ where a is an arbitrary variable.

[4] The word *vired* (pronounced vī-rĕd) has been obtained by spelling backwards, the abbreviation of "derivative."

From definition (7)[5] together with the mathematics of partial derivatives, the following relationships are proven:

$$dx_y = -dy_x \tag{8}$$

and

$$dx_y/dz_y = (\partial x/\partial z)_y, \tag{9}$$

where z is another thermodynamic function.

Ninety vireds may be formed from the ten functions. However, by a simple method of manipulation to be presented below, any vired may be expressed in terms of a few, more "basic" vireds.

We define a basic vired as one composed of any two of the four functions, T, P, V, and S. Any other vired may be resolved into terms of the basic vireds by application of elementary operating rules to the definitions of the functions given by (1) to (6) inclusively. These operating rules for vireds, similar to the simple rules of differentiation, are:

For vireds having a given subscript, y,

I. The vired composed of a single function is zero. Thus $dy_y = 0$.

II. The vired of a sum of variables is the sum of the vireds of the variables. Thus from (4) $dH_y = d(U+PV)_y = dU_y + d(PV)_y$.

III. The vired of a product of two variables is the sum of each variable times the vired of the other variable. Thus $d(PV)_y = PdV_y + VdP_y$.

These rules can be readily proven mathematically with the use of definition (7).

There are twelve basic vireds. Six of these have been resolved through mathematical derivation into simple terms as tabulated below.

$$dT_P = 1 = \frac{T}{C_V} dS_P,$$

$$dT_V = \left(\frac{\partial V}{\partial P}\right)_T = \frac{T}{C_P} dS_V,$$

$$dV_P = \left(\frac{\partial V}{\partial T}\right)_P = dS_T.$$

[5] Definition (7) for $y = P$ gives an indeterminate form $dx_P = -(\partial x/\partial P)_P(\partial P/\partial T)_P$. To solve this form it is first shown mathematically that $-(\partial x/\partial P)_y(\partial y/\partial T)_P$, the definition of the general vired dx_y, is equal to $-(\partial x/\partial P)_T(\partial y/\partial T)_P + (\partial x/\partial T)_P(\partial z/\partial P)_T$. Then for $y = P$, $dx_P = 0 + (\partial x/\partial T)_P$. Hence for further derived proofs, dx_P is taken equal to $(\partial x/\partial T)_P$.

The other six basic vireds can be obtained from this table by use of equality (8). All other vireds can be expressed in terms made up of these twelve vireds and the four functions, T, P, V, and S. It then becomes obvious when noting Eq. (9) that all of the 720 possible partial derivatives of the ten thermodynamic can be expressed in terms of T, P, V and S, together with the specific heats, C_P and C_V, and the easily measurable partial derivatives, $(\partial V/\partial P)_T$ and $(\partial V/\partial T)_P$.

For example, to obtain the partial derivative $(\partial A/\partial S)_V$ express it as the vired quotient dA_V/dS_V. From the table it can be seen that $T/C_V dS_V = (\partial V/\partial P)_T$.

Therefore $$dS_V = \frac{C_V}{T}\left(\frac{\partial V}{\partial P}\right)_T.$$

Since

$A = U - TS$ from (5)

$dA_V = dU_V - d(TS)_V$ Rule II

$dA_V = dU_V - (TdS_V + SdT_V)$ Rule III

$= (TdS_V - PdV_V) - (TdS_V + SdT_V)$ from (3) and II

$= TdS_V - 0 - TdS_V - SdT_V$ Rule I

$= -SdT_V = -S(\partial V/\partial P)_T$ from table.

Therefore

$$\left(\frac{\partial A}{\partial S}\right)_V = \frac{dA_V}{dS_V} = \frac{-S(\partial V/\partial P)_T}{(C_V/T)(\partial V/\partial P)_T} = -\frac{ST}{C_V}.$$

The most complex vired is of the form dF_x, where x is some other function not basic. Consider for example the vired dF_U.

$dF_U = dU_U + d(PV)_U - d(TS)_U$ from (6) and Rule II

$= 0 + PdV_U + VdP_U - TdS_U - SdT_U$ Rule III

$= -PdU_V - VdU_P + TdU_S + SdU_T$ from (8)

$= -P(TdS_V - PdV_V) - V(TdS_P - PdV_P) + T(TdS_S - PdV_S) + S(TdS_T - PdV_T)$ from (3) and II

$= -PTdS_V + 0 - VTdS_P + VPdV_P + 0 - TPdV_S + STdS_T - SPdV_T$ from Rule I.

Since $dV_S = -dS_V$ the first and fourth sig-

nificant terms cancel, $dF_U = -VTdS_P + VPdV_P + STdS_T - SPdV_T$. By substitution from the table,

$$dF_U = -VT\left(\frac{C_P}{T}\right) + VP\left(\frac{\partial V}{\partial T}\right)_P + ST\left(\frac{\partial V}{\partial T}\right)_P + SP\left(\frac{\partial V}{\partial P}\right)_T$$

$$= -VC_P + [VP + ST]\left(\frac{\partial V}{\partial T}\right)_P + SP\left(\frac{\partial V}{\partial P}\right)_T .$$

The method presented here is mathematically exact. It emphasizes the interrelationships between the partial derivatives of the thermodynamic functions. Any partial derivative containing a function not already considered can be determined by the method providing the new function is expressible in terms of the ten functions used here.

Should it be desired to express the partial derivatives in terms other than used here, the expressions for basic vireds tabulated above need only be changed mathematically into the terms wanted.

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Studies in the Autoxidation of Monolayers

I. The Mechanism of Autoxidation of Maleic Anhydride β-Elaeostearin

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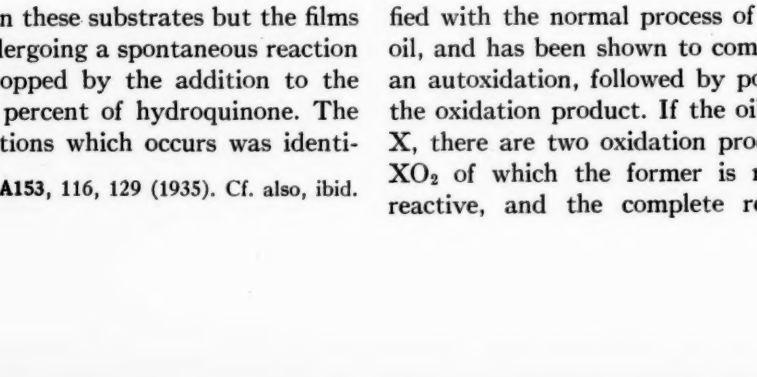
(Received August 2, 1937)

The autoxidation of monolayers of maleic anhydride β-elaeostearin is examined in detail and a free radical mechanism proposed. The effect of temperature and pressure on the rate of oxidation over a very wide *p*H range has been investigated, and the variation of oxidation rate with *p*H shown to be of the form to be anticipated from the postulated mechanism. The absolute values of such constants as can be separately determined are consistent with the physical picture of the process.

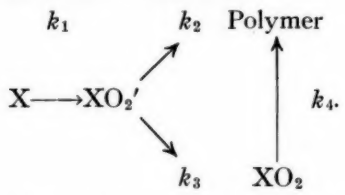
IN two earlier papers[1] a general account has been given of an investigation of the reactions which occur in monolayers of maleic anhydride β-elaeostearin spread on $N/100$ H_2SO_4 or HCl. This material



spreads readily on these substrates but the films are unstable, undergoing a spontaneous reaction which can be stopped by the addition to the substrate of 0.1 percent of hydroquinone. The sequence of reactions which occurs was identified with the normal process of "drying" of an oil, and has been shown to comprise essentially, an autoxidation, followed by polymerization of the oxidation product. If the oil be denoted by X, there are two oxidation products XO_2' and XO_2 of which the former is much the more reactive, and the complete reaction can be

[1] Proc. Roy. Soc. **A153**, 116, 129 (1935). Cf. also, ibid. **155**, 692 (1936).

represented schematically thus:



In the previous papers methods were described by which the four velocity constants can be separately determined, and we shall now examine in more detail the oxidation stage.

We confine our attention to the reaction $X \xrightarrow{k_1} XO_2'$ which represents the autoxidation of the double bond remote from the glyceride residue. The measurements employed in the following discussion were made in the same way as those described previously, i.e., by observing the expansion of a unimolecular film held at a constant surface pressure.

It has already been shown that compression of a film of maleic anhydride β-elaeostearin causes a marked decrease in the velocity of oxidation, the velocity on $N/100$ H_2SO_4 at a surface pressure $F=10$ dynes/cm being only 10 percent of the velocity at $F=6$ dynes/cm. The analogy with the effect of pressure on the rate of oxidation of monolayers of oleic acid on acid $KMnO_4$ was pointed out, and it is clear in this latter case that compression removes the double bonds from the surface and thus from the sphere of action of the oxidizing agent. The mechanism by which compression can retard an autoxidation is less evident. It appears doubtful whether the simple addition of a molecule of oxygen to the double bond is a mechanism capable of giving an adequate account of the experimental results. The alternative conclusion that the substrate plays some essential part in the oxidation is confirmed by some experiments on the effect of *p*H, on the oxidation rate, the results of which are shown in Fig. 1. Curves are drawn for the two temperatures 4°C and 17°C and cover the range of *p*H from −0.7 to +12.0, the actual substrates employed at different parts of the *p*H range being

*p*H < 5	HCl or H_2SO_4.
5–8	phosphate buffers.
8–12	borate—NaOH buffers.

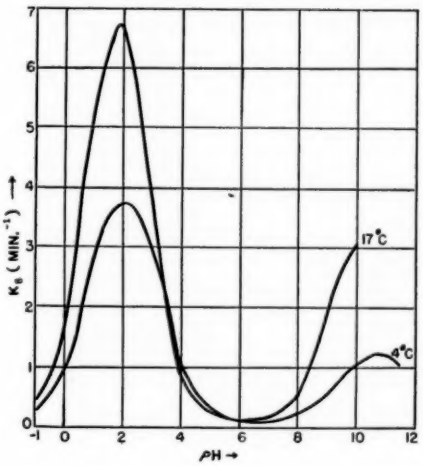


FIG. 1. Effect of *p*H on rate of oxidation at $F=8$.

No significant differences were found when two substrates of the same *p*H but different composition were compared, and it was further shown that addition of a large amount of Na_2SO_4 to a $N/100$ H_2SO_4 substrate did not appreciably affect the rate of oxidation. The experimental results are therefore to be explained in some way purely on the basis of the *p*H variation.

We have thus shown that the substrate is involved in the oxidation and that *p*H has a profound effect, while we may note also that the reproducibility of the results is too good for any explanation based on the adventitious presence of a catalyst to be considered. The effective oxidizing agent cannot therefore contain any element other than oxygen and hydrogen and we are thus led to regard the oxidation as involving almost certainly a free radical mechanism.[2] The electron affinities of the oxygen molecule and some of its reduction products have been estimated by Weiss,[3] as follows:

O_2	2.7 volts
OH	3.7 volts
HO_2	4.6 volts.

The most effective oxidizing agent is therefore the HO_2 free radical which exists in solution in

[2] For general discussions of free radical mechanisms of oxidation see Franck and Haber, Sitzungsber. Akad. Berlin, physik-math. Kl. **33**, 250 (1931). Haber and Willstätter, Ber. **64**, 2844 (1931). Haber and Weiss, Naturwiss. **20**, 948 (1932). Weiss, ibid. **23**, 64 (1935); Nature **133**, 648 (1934). Rice and Rice, *Aliphatic Free Radicals* (1935), pp. 165–182.

[3] Trans. Faraday Soc. **31**, 966 (1935).

equilibrium with the ion O_2', the first reduction product of the oxygen molecule:[4]

$$HO_2 \rightleftharpoons H^+ + O_2'.$$

It has been shown by Haber and Weiss[5] that this equilibrium is important in the catalytic decomposition of H_2O_2, and these workers have been able to estimate the dissociation constant at 20°C as being of the order of 10^{-6}.

If now HO_2 is the effective oxidizing agent in the reaction under consideration we have to suggest some mechanism by which the oxygen molecule can be reduced to O_2'. In the presence of an easily oxidized metal such as $Fe^{\cdot\cdot}$ the process might be written:[6]

$$Fe^{\cdot\cdot} + O_2 \rightleftharpoons Fe^{\cdot\cdot\cdot} + O_2'.$$

We have already concluded that the mechanism does not involve traces of impurity, so that the electron required to reduce the oxygen molecule must be derived from the film material itself. We note that evidence has been brought forward by Morrell and Davis[7] and Hughes[8] that the reactive double bond in maleic anhydride β-elaeostearin is strongly polar, as we should indeed expect from its proximity to the maleic anhydride residue. Many addition reactions of unsaturated compounds can be readily explained by supposing the attack to be made by an ion, which attaches itself to the polar double bond.[9] Thus Moelwyn-Hughes and Legard[10] have shown by a kinetic study that the addition of iodine to aqueous solutions of sodium β-phenylpropiolate takes place in the form of either I_3' or OI'. We are thus led to the suggestion that in the monolayer the double bond will form a complex with the elements of water in the ionic form:

$$R_1CH : CHR_2 + H^+ \; \overset{-}{O}H \rightleftharpoons \underset{\overset{-}{O}H \quad H^+}{R_1CH : CHR_2}.$$

Now this complex contains an electron which is much more readily removable than one of the double bond electrons, for its ionization potential should not differ widely from the figure of 3.7 volts quoted above for the electron affinity of the OH free radical, and we have the possibility of the reaction

$$\underset{\overset{-}{O}H \quad H^+}{R_1CH : CHR_2} \rightarrow \underset{OH \quad H^+}{R_1CH : CHR_2} + e.$$

The complex is therefore oxidizable by molecular oxygen under the experimental conditions to give a free radical complex $\underset{OH \quad H^+}{R_1CH : CHR_2}$ and O_2'. The latter will react with H^+ to give HO_2, and the oxidation to the final peroxide can be readily completed by the interaction of these free radicals. We thus arrive at the following formulation of the oxidation process:

$$\left.\begin{array}{lll} \underset{\overset{-}{O}H \quad H^+}{R_1CH : CHR_2} + O_2 \rightleftharpoons \underset{OH \quad H^+}{R_1CH : CHR_2} + O_2' & (1) & \\ O_2' + H^+ \rightleftharpoons HO_2 & (2) & \\ \underset{OH \quad H^+}{R_1CH : CHR_2} + HO_2 \rightarrow \underset{\diagdown \; \diagup \; O_2}{R_1CH - CHR_2} + H_2O + H^+ & (3) & \end{array}\right\}. \quad (1)$$

This view of the oxidation process enables us to understand the observation of Hughes and Rideal[11] that the oxidizability of a series of unsaturated compounds examined by them depends on the polarity of the double bond, the rate of oxidation being greatest for a β-iso-

[4] The evidence for the existence in solution of this radical and its ion has been summarized by Weiss, Trans. Faraday Soc. **31**, 668 (1935).
[5] Proc. Roy. Soc. **A147**, 332 (1934).
[6] Cf. Weiss, Nature **133**, 648 (1934). See also Part II (below).
[7] Trans. Faraday Soc. **32**, 209 (1936).
[8] J. C. S. 338 (1933).
[9] For a general discussion, see: Robinson, *Outline of an Electrochemical Theory of the Course of Organic Reactions* (Inst. of Chem., 1932). Ingold, Chem. Rev. **15**, 225 (1934).
[10] J. C. S. 424 (1933).
[11] Proc. Roy. Soc. **A140**, 253 (1933).

oleic acid, in which the measured dipole moment of the double bond is highest, and least for oleic and petroselenic acids, in which the dipole moment is very much smaller.

It is clear that the formation of the complex and presumably also the ease of removal of an electron depend on the polarity of the double bond, and one would anticipate furthermore that oxidation of an unsaturated compound in an anhydrous nonpolar solvent would be very slow. It is in fact known that linseed oil which oxidizes at a barely perceptible rate in solvents such as benzene and carbon tetrachloride, is much more readily oxidizable in acetic acid solution.[12]

The mechanism suggested above is therefore in accord with experimental observations other than those it was devised to explain, and we may proceed to examine its kinetic implications.

We suppose the whole of the film material to be in the form of the complex and denote its concentration by c_1, while the concentration of the free radical complex $R_1CH : CHR_2$ is denoted by c_2. The velocity constants of the forward reaction are written k_x where x is the number of the appropriate equation; the reverse reactions are similarly denoted by k_{xr} and equilibria by k_{xe}, Eq. (2) represents an equilibrium which has already been studied by Haber and Weiss[5] and its equilibrium constant k_{2e} is given by

$$k_{2e}=[O_2'][H^+]/[HO_2]. \qquad (2)$$

The velocity of oxidation is V, where

$$V=k_3c_2[HO_2]. \qquad (3)$$

Writing down the stationary state equation for the free radical complex and combining with (2) and (3) we find for the rate of oxidation:

$$V=\frac{k_1c_1[O_2][H^+]}{[H^+]+k_{1r}k_{2e}/k_3}. \qquad (4)$$

If K is the measured unimolecular velocity constant

$$V=Kc_1[O_2] \qquad (5)$$

and

$$K=\frac{k_1[H^+]}{[H^+]+k_{1r}k_{2e}/k_3}. \qquad (6)$$

For small values of $[H^+]$, $K : [H^+]$. For large values of $[H^+]$, K is independent of $[H^+]$.

This mechanism is clearly inadequate to account for the complexity of the effect of *p*H (Fig. 1) and in fact represents adequately only that portion of the curves lying in the *p*H range 5~2; but it is not difficult to see what modifications are required. We have so far assumed that the unoxidized film is always in the form $R_1\underset{OH}{\underline{C}}H : CHR_2$, but it is clear that this is only likely to be the case on substrates not far removed from neutrality where the concentrations of both H^+ and OH' are reasonably large. At higher or lower *p*H's we shall expect to obtain a change in the nature of the film, represented by Eqs. (7):

$$\left.\begin{aligned} R_1\underset{OH}{\underline{C}}H : CHR_2+H^+ &\rightleftharpoons R_1CH : CHR_2+H_2O \quad (4)\\ R_1\underset{OH}{\underline{C}}H : CHR_2+OH' &\rightleftharpoons R_1\underset{OH}{\underline{C}}H : CHR_2+H_2O \quad (5)\end{aligned}\right\}. \qquad (7)$$

On acid substrates we thus obtain a complex which no longer contains a hydroxyl ion and has therefore no readily available electron, so that the observed stability of the film on strongly acid substrates is to be anticipated. On alkaline substrates on the other hand we produce a second complex, capable of autoxidation at a rate which will probably differ from that found for the neutral complex. We shall have a further set of reactions analogous to (1):

[12] Cf. Ueno, Okamura and Saida, J. Soc. Chem. Ind. Japan **34**, 106B (1931).

$$\left.\begin{array}{ll} R_1CH:CHR_2 \quad\quad R_1CH:CHR_2 & \\ \quad\quad\; +O_2 \rightleftharpoons \quad\quad\; +O_2' & (6) \\ \quad OH \quad\quad\quad\; OH & \\ O_2'+H^+ \rightleftharpoons HO_2 & (2) \\ R_1CH:CHR_2 & \\ \quad\quad +HO_2 \rightarrow R_1CH-CHR_2+H_2O & (7) \\ \quad OH \quad\quad\quad\quad\; O_2 & \end{array}\right\} \quad (8$$

To obtain the complete variation of K with pH we have now to combine Eqs. (1), (7) and (8). Eq. (2) will still hold, and we shall have two further equilibria:

$$k_{4e}=c_1[H^+]/c_3. \quad (9)$$

$$k_{5e}=c_1[OH']/c_4. \quad (10)$$

where c_3 and c_4 are the respective concentrations of $R_1CH:CHR_2$ and $R_1\underset{OH}{\overset{H^+}{C}}H:CHR_2$. If further c_5 is the concentration of $R_1\underset{OH}{CH}:CHR_2$, the velocity of oxidation V is given by

$$V=(k_3c_2+k_7c_5)[HO_2]. \quad (11)$$

The unoxidized film is now regarded as a mixture, its total concentration c is

$$c=c_1+c_3+c_4. \quad (12)$$

Eq. (5) must also be rewritten as

$$V=Kc[O_2]. \quad (13)$$

It is easily shown that

$$V=\frac{k_1c_1[O_2][H^+]}{[H^+]+k_{1r}k_{2e}/k_3}+\frac{k_6c_4[O_2][H^+]}{[H^+]+k_{6r}k_{2e}/k_7}. \quad (14)$$

We have now to evaluate c_1 and c_4 in terms of c and $[H^+]$, which can be done by combining Eqs. (9), (10) and (12), when we readily find:

$$c_1=\frac{c}{1+[H^+]/k_{4e}+[OH']/k_{5e}}, \quad (15)$$

$$c_4=\frac{c[OH']/k_{5e}}{1+[H^+]/k_{4e}+[OH']/k_{5e}}. \quad (16)$$

Writing $$[H^+][OH']=k_w \quad (17)$$

we substitute these values in (14) and combine (13) to obtain:

$$K=\frac{[H^+]}{k_w/k_{5e}+[H^+]+[H^+]^2/k_{4e}} \times\left\{\frac{k_1[H^+]}{[H^+]+k_{1r}k_{2e}/k_3}+\frac{k_6k_w/k_{5e}}{[H^+]+k_{6r}k_{2e}/k_7}\right\}, \quad (18)$$

which is of the form:

$$K=\frac{[H^+]}{A+[H^+]+B[H^+]^2} \times\left\{\frac{c[H^+]}{[H^+]+D}+\frac{E}{[H^+]+F}\right\}, \quad (19$$

where
$$\begin{aligned} A&=k_w/k_{5e}, & D&=k_{1r}/k_{2e}, \\ B&=1/k_{4e}, & E&=k_6k_w/k_{5e}, \\ C&=k_1, & F&=k_{6r}k_{2e}/k_7. \end{aligned} \quad (20)$$

Eq. (19) may be somewhat simplified to an empirical form which satisfactorily describes the experimental results. It is clear that since the range of $[H^+]$ covered is from 5 to 10^{-12} the various constants will not in general be important at the same pH's, and we can in fact divide K into two portions K_a and K_b representing respectively the acid and alkaline sides of neutrality. On the acid side,

$$\frac{E}{[H^+]+F}\ll\frac{C[H^+]}{[H^+]+D} \quad \text{and} \quad A\ll[H^+],$$

so that

$$K_a=\frac{C[H^+]}{(1+B[H^+])([H^+]+D)}. \quad (21)$$

On the alkaline side,

$$\frac{C[H^+]}{[H^+]+D} \ll \frac{E}{[H^+]+F} \quad \text{and} \quad B[H^+] \ll 1,$$

so that

$$K_b = \frac{E[H^+]}{(A+[H^+])([H^+]+F)}. \qquad (22)$$

K_a and K_b thus vary in the same way with $[H^+]$, showing maxima at $[H^+]=(D/B)^{\frac{1}{2}}$ and $(AF)^{\frac{1}{2}}$, respectively.

The maximum on the acid side is found at about *p*H2, but the position of the corresponding maximum on the alkaline side is very difficult to determine owing to experimental difficulties. At very high *p*H's hydrolysis occurs at a rate comparable with that of the oxidation, while even before this point is reached there is a large expansion of the film which leads to a complication. We have already seen[1] that the oxidation is faster at low pressures than at high, and it is clear that this expansion of the film at high *p*H's will have an effect similar to that produced by a decrease of pressure. By combining the known effect of pressure on the velocity constant with the *F–A* curve of the material it is possible to apply an approximate correction for this expansion, and this has been done in deriving the curves of Fig. 1. The experimental data for *p*H's higher than 10.0 must be regarded as less certain than the remainder and cannot be taken as conclusive proof of the existence of the predicted maximum.

Adding (21) and (22) we obtain an expression which gives an excellent representation of the experimental results, except in the immediate neighborhood of the minimum (nearly neutral substrates) where the velocity is higher than calculated. This residual rate may be introduced empirically as a small correction term K_c, which may be interpreted either as a slow oxidation by a different mechanism or as due to adventitious catalytic impurities (e.g., traces of heavy metals). The lack of reproducibility in this region, combined with the fact that the effect of catalysts is a maximum here gives some indication that the second alternative is the more likely one. We thus obtain finally for the variation of the velocity constant K with $[H^+]$ the following expression

$$K = K_c + \frac{C[H^+]}{(1+B[H^+])(D+[H^+])} + \frac{E[H^+]}{(A+[H^+])(F+[H^+])}. \qquad (23)$$

This equation has been fitted to the experimental results in the following manner:

The oxidation velocity at $F=8$ was measured at a constant temperature (4°C or 17°C) as described previously[1] while the *p*H was varied by changing the substrate, either by injecting acid or alkali, or by a complete change of substrate. The whole range of *p*H was covered three times at each temperature with fresh set-ups of the apparatus, the results being in very satisfactory agreement. Any discrepancies affected only the absolute values of the velocity and not the general shape or position of the curve. A further series of measurements was then carried out at constant *p*H while the temperature was varied, four or five readings being taken over a temperature range of about 20°. From these latter experiments values were calculated for the critical increment at *p*H's 0.3, 2.0, 3.3, 6.4 and 8.5. Eq. (26) was then fitted to the collected results at the two temperatures (4°C and 17°C), particular care being taken to make the calculated critical increments agree with the experimental values. The final values assigned to the various constants are given in Table I, from which K is calculable in min.$^{-1}$. These constants have been employed in calculating the curves of Fig. 1.

No value of A is given for the higher temperature, as it was found impracticable to extend the measurements sufficiently far to obtain the position of the maximum.

In view of the large number of constants it is impossible to obtain very accurate values of any of them, but it may be noted that B and C

TABLE I. *Experimental constants of Eq. (26) at $F=8$.*

	4°C	17°C	E_c (Kcal.)
K_c	0.10	0.15	5.0
A	4×10^{-13}	?	?
B	4.30	3.45	−2.7
C	3.97	7.06	7.0
D	3.5×10^{-4}	9.6×10^{-4}	12.4
E	8.25×10^{-10}	4.8×10^{-9}	21.6
F	7.85×10^{-10}	1.55×10^{-9}	8.4

are well defined and are probably accurate to within 10 percent, the probable errors in the other constants are larger, and A—which depends entirely on the position of the maximum on the alkaline side—is very uncertain.

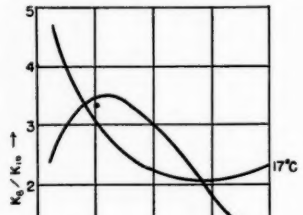


FIG. 2. Effect of pressure on oxidation rate.

We see by inspection of Eq. (20) that the constants B and C give us $1/k_{4e}$ and k_1, and the corresponding energies of activation. Now k_1 is the measured velocity constant of the primary interaction of oxygen with the film and is therefore calculable by the ordinary methods of kinetics. The process may be pictured as involving the collision of an oxygen molecule from the air with a double bond in the surface, and we can therefore set the reaction rate equal to the collision number multiplied by $e^{-E/RT}$ where $E=7.0$ Kcal./g mole (Table I), the steric factor being assumed to be unity.

The number (Z) of molecules of molecular weight M hitting 1 cm^2 of surface per second is given by.[13]

$$Z=n(RT/2\pi M)^{\frac{1}{2}}.$$

Take the target area of a double bond as 20 A^2 it is easily shown that the observed unimolecular constant k_1 is:

$$k_1=0.10 \text{ sec.}^{-1}=6.0 \text{ min.}^{-1}.$$

This is to be compared with the observed value of 7.06 min.$^{-1}$; the agreement is good and gives considerable additional support to the postulated reaction mechanism.

Analysis of the absolute values of the other constants is less certain. From (19) we note that k_6 is given by the ratio E/A, so that at 4°C k_6 is approximately 2000 min.$^{-1}$. Now k_6 is the velocity constant of a reaction precisely similar to the one we have just considered, so that k_6 should be calculable in the same way as k_1, and we shall have

$$k_6/k_1=e^{(E_1-E_6)/RT}. \tag{24}$$

Inserting values of k_1, k_6 and E_1 we obtain an estimate of $E_6\sim 3.6$ Kcal./mole.

Another possible method of determining the constants A and B has been considered. The transition of the film material from a neutral to an acid or alkaline complex should be accompanied by a change of the surface potential ΔV, which could thus be employed to determine the pH's at which these changes are half-complete. These are, respectively, $[H^+]=1/B$; $[H^+]=A$. Two difficulties were encountered which prevented this method from being applied. It has been shown by Schulman and Hughes[14] that all oxygen compounds show a large rise of ΔV on strongly acid substrates, a behavior which they ascribed to the formation of oxonium compounds. The pH at which the transition neutral complex$\rightleftharpoons$acid complex should occur coincides with that of oxonium formation, so that the phenomenon it was desired to measure is completely masked. On the alkaline side it was found impossible to obtain reliable values of ΔV at sufficiently high pH's to permit the method to be used.

The remaining constants D and F each involve three constants which are not separately determinable, even if Haber and Weiss' estimate of k_{2e} is assumed. In any event these constants are not known with sufficient accuracy to justify further discussion.

Effect of Pressure

The measurements considered so far were all made at a pressure $F=8$ dynes/cm, this value having been chosen because experimentally it is found possible to obtain more reliable results at $F=8$ than at any higher or lower pressure. In attempting to investigate quantitatively the effect of pressure we therefore approach the limits of the experimental technique, especially as the range of pressure over which any oxidation velocity constants can be obtained is very

[13] Tolman, *Statistical Mechanics* (1927), p. 206.

[14] Proc. Roy. Soc. **A138**, 430 (1932).

narrow. A series of measurements has been carried out on acid substrates at $F=10$, at the two temperatures 4°C and 17°C, analogous to the series at $F=8$. The general effect of increasing the pressure from $F=8$ to 10 is to depress the whole of the $K\sim p$H curve, but there is in addition a tendency to displace the maximum to a higher pH (especially at 4°C) and to produce a flatter maximum. In Fig. 2 the results of this series of experiments are summarized by plotting the ratio K_8/K_{10} as a function of pH at each temperature, and it will be noted that the inhibitory effect of pressure disappears for substrates of pH 4 at 4°C. It was found impossible to obtain data sufficiently reliable to permit the quantitative analysis of the effect of pressure of the individual constants.

We may conclude finally that the reaction mechanism which has been put forward gives a satisfactory account of the effect of pH in the velocity of oxidation of monolayers of maleic anhydride β-elaeostearin, although it has not been found possible to make the experimental accuracy sufficiently high to permit a complete quantitative analysis of the effects of temperature and pressure on the separate reactions involved.

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Studies in the Autoxidation of Monolayers

II. Catalysts and Inhibitors

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An account is given of the effect of metallic catalysts and organic pro- and anti-oxygens added to the substrate on the rate of oxidation of monolayers of maleic anhydride α-elaeostearin. The catalytic effect depends both in direction and magnitude on the pH of the substrate. The results are discussed in the light of the autoxidation mechanism proposed in Part I, and a semi-quantitative kinetic treatment developed which accounts successfully for the principal features of the results.

IN discussing the general behavior of monolayers of maleic anhydride β-elaeostearin it it was noted[1] that the oxidation process is accelerated by adding to the substrate a small amount of $CoSO_4$, and retarded by a similar addition of hydroquinone. In this paper we shall examine these effects in more detail, especially in the light of the oxidation mechanism discussed above.

METALLIC CATALYSTS

The experiments to which reference has been made were concerned with the effect of $CoSO_4$ on the rate of oxidation on $N/100$ H_2SO_4 substrates, and the behavior found was entirely in accord with expectation, the oxidation rate increasing progressively as the cobalt concentration was raised. Replacement of cobalt by other metals however leads to more complex results. Thus $MnSO_4$ in $N/100$ H_2SO_4 gives only small accelerations, while high concentrations cause a reversal of the sign of catalysis, the metal becoming an inhibitor. Similar results were found for lead acetate in $N/100$ acetic acid and also for $CoSO_4$ in $N/10$ H_2SO_4, while $CoSO_4$ in $N/100$ acetic acid gives more marked catalysis. It is evident that the catalytic effect of metals is complicated and is a function of both the concentration of the metal and the pH of the substrate. We have now to enquire therefore whether this behavior can be explained on the basis of the reaction mechanism given above, and we shall consider $Co^{\cdot\cdot}$ as a typical example. No experiments have been made on alkaline substrates so that the only oxidizable

[1] Proc. Roy. Soc. **A153**, 123 (1900).

material to be considered is $R_1CH(\bar{O}H) : CHR_2(H^+)$. As an additional simplification we shall restrict our attention to pH < 2, so that the concentration of the acid complex can be neglected, and the unoxidized film treated as consisting entirely of the neutral complex. The positive catalytic effect of the metal we shall represent in the usual way as an alternative oxidation of the metal (by air) and reduction (by the film), while the negative catalytic effect is most simply accounted for by loss of HO_2 by oxidizing the metal. Combining these reactions with the normal oxidation mechanism we obtain the following set of reactions:[2]

$$\left.\begin{array}{ll}
R_1CH(\bar{O}H) : CHR_2(H^+) + O_2 \rightleftharpoons R_1CH(OH) : CHR_2(H^+) + O_2' & (1)\\
O_2' + H^+ \rightleftharpoons HO_2 & (2)\\
R_1CH(OH) : CHR_2(H^+) + HO_2 \rightarrow R_1CH(O_2)CHR_2 + H_2O + H^+ & (3)\\
Co^{\cdot\cdot} + O_2 \rightleftharpoons Co^{\cdot\cdot\cdot} + O_2' & (8)\\
R_1CH(OH) : CHR_2(H^+) + Co^{\cdot\cdot\cdot} \rightleftharpoons R_1CH(OH) : CHR_2(H^+) + Co^{\cdot\cdot} & (9)\\
Co^{\cdot\cdot} + HO_2 \rightarrow Co^{\cdot\cdot\cdot} + HO_2' & (10)
\end{array}\right\}. \quad (1)$$

(Followed by $HO_2' + H^+ \rightleftharpoons H_2O_2$, and the catalytic decomposition of the H_2O_2 produced.)

These reactions are now to be analyzed kinetically so as to obtain an expression for the oxidation rate V, in terms of the concentration (c) of $R_1CH(OH^-) : CHR_2(H^+)$, $[O_2]$, $[H^+]$ and the concentration (c_c) of cobalt added. The derivation follows the same general method as has been employed in Part I, and will only be given in outline. The unknowns which have to be eliminated are $[O_2']$, $[HO_2]$, $[Co^{\cdot\cdot}]$, $[Co^{\cdot\cdot\cdot}]$ and c_2, the concentration of $R_1CH(OH) : CHR_2(H^+)$. The five equations necessary are obtained by writing down:

(i) the dissociation equilibrium of HO_2

(ii), (iii), (iv), stationary state equations for HO_2, O_2' and $R_1CH(OH) : CHR_2(H^+)$

(v) $[Co^{\cdot\cdot}] + [Co^{\cdot\cdot\cdot}] = c_c$.

A slight simplification is introduced by writing c_c instead of $[Co^{\cdot\cdot}]$ in obtaining the rate of reaction (10). The problem is readily reduced to the following quadratic equation for $[HO_2]$:

$$[HO_2]^2 \cdot x \cdot \frac{k_{2e}k_{8r}}{[H^+]}\left(1 + \frac{k_{1r}k_{2e}}{k_3[H^+]}\right) + [HO_2]\left[\left(k_9c + \frac{k_{9r}}{k_3}x\right)\left(\frac{k_{1r}k_{2e}}{k_3[H^+]}x + k_2k_{2e} - k_{2r} + \frac{k_{2e}k_{8r}}{[H^+]}c_c\right)\right.$$

$$\left. - \frac{k_{2e}k_{8r}}{[H^+]}c(k_1[O_2] + k_9c_c) + k_8x[O_2]\left(1 + \frac{k_{1r}k_{2e}}{k_3[H^+]}\right)\right] - c \cdot [O_2]\left\{k_1k_9c + \frac{k_1k_{9r}}{k_3}x + k_1k_8[O_2] + k_8k_9c_c\right\} = 0, \quad (2)$$

where
$$x = k_3c_2 = k_2k_{2e} - k_{2r} - k_{10}c_c. \quad (3)$$

The velocity of oxidation is given by

$$V = k_3c_2[HO_2] = x[HO_2]. \quad (4)$$

[2] The nomenclature adopted is the same as in Part I (*q.v.*) and identical reactions are given the same number in both papers.

Also, from Eq. (5) of part I we know that the rate of oxidation V_0 in the absence of catalyst is given by

$$V_0=\frac{k_1c[O_2][H^+]}{[H^+]+k_{1r}k_{2e}/k_3}. \tag{5}$$

We now employ Eqs. (4) and (5) to change the variable in Eq. (2) from $[HO_2]$ to K/K_0, remembering that $V/V_0=K/K_0$, by the substitution

$$[HO_2]=\frac{K}{K_0}\cdot\frac{k_1k_3c[O_2][H^+]}{x(k_{1r}k_{2e}+k_3[H^+])}. \tag{6}$$

We thus obtain the following quadratic equation for K/K_0:

$$\left(\frac{K}{K_0}\right)^2\cdot\frac{k_1^2k_{2e}k_{8r}c[O_2]}{x}+\frac{K}{K_0}\cdot\frac{k_1}{x}\left[\left(k_9c+\frac{k_{9r}}{k_3}x\right)\left\{x\left([H^+]+\frac{k_{1r}k_{2e}}{k_3}\right)+c_c(k_{10}[H^+]+k_{2e}k_{8r})\right\}\right.$$
$$\left.-k_{2e}k_{8r}c(k_1[O_2]+k_9c_c)+k_8x[O_2]\left([H^+]+\frac{k_{1r}k_{2e}}{k_3}\right)\right]-\left([H^+]+\frac{k_{1r}k_{2e}}{k_3}\right)$$
$$\times\left\{k_1k_9c+\frac{k_1k_{9r}}{k_3}x+k_1k_8[O_2]+k_8k_9c_c\right\}=0. \tag{7}$$

This equation is now to be used to discuss the variation of the catalytic effect as a function of $[H^+]$ and c_c.

Variation with *p*H

At constant c_c, (7) may be written in the empirical form:

$$(K/K_0)^2+(K/K_0)(A+B[H^+])-(D+E[H^+])=0, \tag{8}$$

where A, B, D, E are independent of $[H^+]$. This may be further modified by changing to a new variable

$$Y=(K/K_0)-1 \tag{9}$$

when we obtain an equation of the same form as (8):

$$Y^2+Y(A'+B'[H^+])-(D'+E'[H^+])=0. \tag{10}$$

As $c_c\to0$, $Y\to0$ so that for small values of c_c the solution of (10) is

$$Y\doteqdot\frac{D'+E'[H^+]}{A'+B'[H^+]}. \tag{11}$$

This equation requires that the catalytic effect of the metal will, in general, be a function of *p*H, but does not enable us to predict the direction of the effect. In order to apply it to the experimental data it is necessary to compare values of Y at the same (very small) value of c_c and this is most conveniently done by comparing values of

$$\left(\frac{\partial(K/K_0)}{\partial c_c}\right)_{c_c=0}$$

at different *p*H's. It is clear that the variation should be of the form

$$\left(\frac{\partial(K/K_0)}{\partial c_c}\right)_{c_c=0}=\frac{\alpha+\beta[H^+]}{\gamma+[H^+]}, \tag{12}$$

where α, β, γ are constants. In Fig. 1 plots of

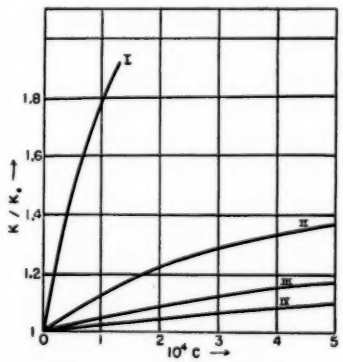

FIG. 1. Effect of *p*H on catalytic. Effect of cobalt. I, *p*H 4.7; II, 3.8; III, 3.0; IV, 2.0.

TABLE I. *Variation of catalytic effect with pH.*

[H⁺]	$\left(\frac{\partial(K/K_0)}{\partial c_c}\right)_{c_c=0}$		[c_c in g % Co⁺⁺]
	obs.	*calc.*	
2.0×10^{-5}	12,000	12,000	
1.6×10^{-4}	2,000	2,060	
1.0×10^{-3}	450	495	
1.0×10^{-2}	250	230	

K/K_0 against c are given for a number of pH's, and in Table I the observed values of

$$\left(\frac{\partial(K/K_0)}{\partial c_c}\right)_{c_c=0}$$

are compared with the values calculated from Eq. (12) by putting $\alpha=0.298$, $\beta=200$, $\gamma=5\cdot2\times10^{-6}$. The agreement is certainly within experimental error over the range of pH 2.0 to 4.7. It was not found practicable to extend the measurements to higher pH's as it was impossible to obtain sufficiently consistent velocity constants in this region, probably owing to the presence of traces of metallic impurity in the substrate. (At pH 5.3, a 10 percent acceleration would be produced by the presence of 3×10^{-6} percent Co.).

Effect of Cobalt Concentration

We have next to enquire whether the observed change of sign of catalysis at high metal concentrations is also explicable by this analysis. For this purpose Eq. (7) may be rewritten to give K/K_0 as an empirical function of c_c, in the form

$$(K/K_0)^2+(K/K_0)(A+B\cdot c_c+D\cdot c_c^2) -(E+F\cdot c_c+G\cdot c_c^2)=0, \quad (13)$$

where A, B, D, E, F, G are independent of c_c. The condition for a reversal of sign of catalysis is given by $K/K_0=1$, whence

$$1+A-E+(c_c)_r(B-F)-(c_c)_r^2(G-D)=0, \quad (14)$$

where $(c_c)_r$ is the value of c_c for $K/K_0=1$. Also since $(c_c)_r=0$ must be a solution of (14),

$$E=A+1$$

and we find

$$(c_c)_r=(B-F)/(G-D) \quad \text{(or 0)}. \quad (15)$$

The existence of a critical concentration at which reversal of catalysis occurs is therefore predicted, but it is not possible to predict the variation of $(c_c)_r$ with pH.

Organic Pro- and Anti-Oxygens

The phenomena associated with the use of organic pro- and anti-oxygens in bulk have been widely studied and we are in particular indebted to Moureu and his collaborators[3] for the collection of a great deal of empirical information on this subject. A wide diversity of behavior is shown by the many systems investigated and examples have been found of almost every conceivable type of behavior, including the following:—

(i) Simple acceleration or retardation of the oxidation,

(ii) Acceleration by small amounts of catalyst and retardation by larger amounts, or *vice versa*,

(iii) Reversal, i.e., acceleration during the early stages of the oxidation followed by retardation of the later stages, or *vice versa*.

A few experiments soon showed that the results obtained in monolayers, when pro- and anti-oxygens are added to the substrate, are likely to prove almost as complex, although no example of reversal (class (iii)) has yet been found. Some typical results are given in Fig. 2, in which the effect of concentration on catalytic activity is shown for several oxidation catalysts at pH 1.

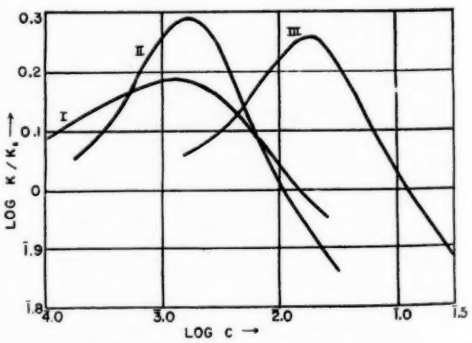

FIG. 2. Effect of organic pro- and anti-oxygens. I, iodoacericacia; II, *p*-nitraniline; III, piperidine.

[3] For reviews see Chem. Rev. **3**, 113 (1926); Chem. and Ind. **47**, 819, 848 (1928).

Instead of examining the behavior of a large number of catalysts it was considered preferable to study a selected system in some detail and the catalyst chosen was hydroquinone, the autoxidation of which has been extensively studied.[4] This material is stable to oxygen at *p*H's below 7, its rate of oxidation being proportional to $[OH']^2$. In terms of a free radical mechanism the oxidative process may be formulated as follows.[5]

$$C_6H_4(OH)_2 \rightleftharpoons C_6H_4O_2'' + 2H^+,$$
$$C_6H_4O_2'' + O_2 \rightleftharpoons C_6H_4O_2' + O_2',$$
$$H^+ + O_2' \rightleftharpoons HO_2,$$
$$C_6H_4O_2'' + HO_2 \rightarrow C_6H_4O_2' + HO_2',$$
$$[H^+ + HO_2' \rightleftharpoons H_2O_2,$$
$$C_6H_4O_2'' + H_2O_2 \rightarrow C_6H_4O_2' + OH' + OH,$$
$$C_6H_4O_2'' + OH \rightarrow C_6H_4O_2' + OH'],$$
$$2C_6H_4O_2' \rightarrow C_6H_4O_2 + C_6H_4O_2''.$$

The bracketed equations we shall omit from our analysis as they introduce no fundamental differences. We have now to formulate the interaction of this system with maleic anhydride β-elaeostearin, and we shall confine ourselves—as in the case of catalysis by cobalt—to the *p*H range 2–7, so that the complete system to be examined is as follows:

$$\left.\begin{array}{lll}
R_1CH:CHR_2 + O_2 \rightleftharpoons R_6CH:CHR_2 + O_2' & (1)\\
\quad\bar{O}H \quad H^+ \qquad\qquad\quad OH \quad H^+ & \\
H^+ + O_2' \rightleftharpoons HO_2 & (2)\\
R_1CH:CHR_2 + HO_2 \rightarrow R_1CH-CHR_2 + H_2O + H^+ & (3)\\
\quad OH \quad H^+ \qquad\qquad\quad \diagdown\,O_2\,\diagup & \\
C_6H_4(OH)_2 \rightleftharpoons C_6H_4O_2'' + 2H^+ & (11)\\
C_6H_4O_2'' + O_2 \rightleftharpoons C_6H_4O_2' + O_2' & (12)\\
C_6H_4O_2'' + HO_2 \rightarrow C_6H_4O_2' + HO_2' & (13)\\
2C_6H_4O_2' \rightarrow C_6H_4O_2 + C_6H_4O_2'' & (14)\\
R_1CH:CHR_2 + C_6H_4O_2' \rightleftharpoons R_1CH:CHR_1 + C_6H_4O_2'' & (15)\\
\quad\bar{O}H \quad H^+ \qquad\qquad\quad OH \quad H^+ &
\end{array}\right\}. \quad (16)$$

Let c_i = concentration of $C_6H_4(OH)_2$,
c_6 = concentration of $C_6H_4O_2''$,
c_7 = concentration of $C_6H_4O_2'$,

the remainder of the nomenclature being as defined above. Since hydroquinone is very slightly ionized in the *p*H range considered c_i may be identified with the total hydroquinone concentration. The analysis follows the same lines as before, the necessary equations being derived by writing down:

(i), (ii) dissociation constants for reactions (2) and (11). (iii), (iv), (v) stationary state equations for $R_1CH:CHR_2$ (OH, H^+), HO_2 and $C_6H_4O_2'$. The problem may now be reduced to an equation for $[HO_2]$ but the expression obtained is much too cumbersome to handle. It can be greatly simplified if we neglect the term in c_7^2, a process which is justified to a first approximation since c_7 is small. The equation now becomes:

$$[HO_2]^2\left\{\frac{k_{2e}k_{12r}(k_{1r}k_{2e}+k_3[H^+])}{k_3k_{15c}[H^+]^2}\left(k_2k_{2e}-k_{2r}-\frac{k_{11e}k_{13}c_i}{[H^+]^2}\right)\right\}+[HO_2]\left\{\left(k_2k_{2e}-k_{2r}-\frac{k_{11e}k_{13}c_i}{[H^+]^2}\right)\right.$$
$$\left.\cdot\frac{1}{k_3[H^+]}\left(k_{1r}k_{2e}+k_3[H^+]+\frac{k_{2e}k_{11e}k_{12r}k_{15r}c_i}{k_{15c}[H^+]^2}\right)-\frac{k_{11e}k_{13}c_i}{[H^+]^2}-\frac{k_1k_{2e}k_{12r}}{k_{15}[H^+]}[O_2]\right\}-[O_2]\left\{k_1c+\frac{k_{11e}k_{12}c_i}{[H^+]^2}\right\}=0. \quad (17)$$

[4] La Mer and Rideal, J. Am. Chem. Soc. **46**, 223 (1924). Reinders and Dingemans, Rec. trav. chim. Pays-bas **53**, 209 (1934).
[5] Cf. Weiss, Naturwiss. **23**, 64 (1935).

A first approximation to the solution of this equation can be obtained by neglecting the term in $[HO_2]^2$, since we know that $[HO_2]$ must be small, and our confidence in this procedure is increased by noting that we obtain the correct value of $[HO_2]_0$ by putting $c_i=0$. From the value of $[HO_2]$ we readily obtain the following expression for the catalytic ratio V/V_0.

$$\frac{V}{V_0}=\frac{(k_3[H^+]+k_{1r}k_{2e})\{k_1c+k_{11e}k_{12}c_i/[H^+]^2\}}{k_1c\left\{k_{1r}k_{2e}+k_3[H^+]+\dfrac{k_{2e}k_{11e}k_{12r}k_{15r}c_i}{k_{15}c[H^+]^2}-\dfrac{k_3}{[H^+]}\dfrac{k_1k_{1r}k_{2e}[H^+][O_2]+k_{11e}k_{13}k_{15}c_i}{k_2k_{2e}-k_{2r}-k_{11e}k_{13}c_i/[H^+]^2}\right\}}. \tag{18}$$

This may be written in the form:

$$\frac{V}{V_0}=\frac{(A+[H^+])(B+D\cdot c_i/[H^+]^2)}{E+F[H^+]+G\cdot\dfrac{c_i}{[H^+]^2}-\dfrac{L+c_i/[H^+]}{M-N\cdot c_i/[H^+]^2}}, \tag{19}$$

where A, B, D, E, F, G, L, M and N do not involve $[H^+]$ or c_i. For small values of c_i we can expand the last term of the denominator. Then collecting similar terms and introducing the condition that $V=V_0$ for $c_i=0$ we obtain finally (writing fresh constants):

$$\frac{V}{V_0}=\frac{(A+[H^+])(1+B\cdot c_i/[H^+]^2}{A+[H^+]+D\cdot c_i/[H^+]+E\cdot c_i/[H^+]^2-F\cdot c_i^2/[H^+]^3}. \tag{20}$$

We have now to employ this equation to discuss the variation of V/V_0 with c_i and $[H^+]$ and we must remember in doing so that the equation has been derived on the basis of two assumptions

(i) that c_i is small,
(ii) that $10^{-2}\ll[H^+]\ll10^{-7}$.

If $[H^+]$ is very small,

$$\frac{V}{V_0}\sim\frac{AB}{E-F\cdot c_i/[H^+]}. \tag{21}$$

At constant c_i, V/V_0 will therefore increase as $[H^+]$ decreases, while at constant $[H^+]$, V/V_0 will increase with c_i. It is clear that this equation is meaningless for $c_i\geq E[H^+]/F$. If $[H^+]$ is large,

$$\frac{V}{V_0}\sim\frac{[H^+]}{[H^+]+D\cdot c_i/[H^+]}. \tag{22}$$

At constant c_i, V/V_0 will therefore increase as $[H^+]$ increases, the limit being given by $V/V_0\rightarrow1$; while at constant $[H^+]$, V/V_0 will decrease as c_i increases.

The condition for a reversal of sign of catalysis is found by putting $V=V_0$ in Eq. (20) and is easily seen to be of the form

$$(c_i)_r=\alpha[H^+]^2+\beta[H^+], \tag{23}$$

where α, β are constants. Combining the various deductions we have been able to make from Eq. (20) we thus reach the following conclusions:

(i) At constant c_i, V/V_0 approaches unity at low pH's, decreases as the pH is raised, passes through a minimum and then increases again, finally becoming >1 at sufficiently high pH's.
(ii) At constant $[H^+]$, the conclusions are less certain, but it seems most probable that the $(V/V_0\sim c_i)$ curve should resemble in general form the $(V/V_0\sim p\mathrm{H})$ curve.

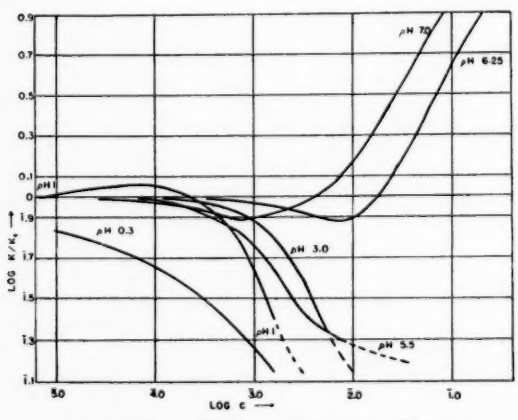

FIG. 3. Effect of hydroquinone on oxidation.

In Figs. 3 and 4 are plotted the results of an extensive series of measurements over a wide range of values of both c_i and $[H^+]$ and we observe that, within the limits defined above, the analysis is fairly successful. The decrease of V/V_0 at low pH's is outside our restricted pH range, but the $(V/V_0 \sim p\text{H})$ curves are in other respects essentially similar to the prediction. In the $(V/V_0 \sim c_i)$ curves a reversal of sign of catalysis is found only for the two highest pH's but there is some evidence of a minimum in the next lowest pH. If we insert the two observed values of $(c_i)_r$ in Eq. (23) we find

$$\alpha = 10^{10}, \qquad \beta = 3 \times 10^4,$$

whence we can calculate $(c_i)_r$ for other pH's, and it is easily seen that for pH 5.5, $(c_i)_r \leqq 0.2$ percent, while for the lower pH's $(c_i)_r$ is impossibly high.

The mechanism advanced in Part I thus gives a reasonably satisfactory account of the behavior of metallic catalysts and organic pro- and anti-oxygens. The treatment given, while only approximate, nevertheless elucidates the principal features of the experimental results, and thus increases our confidence in the essential correctness of the mechanism proposed.

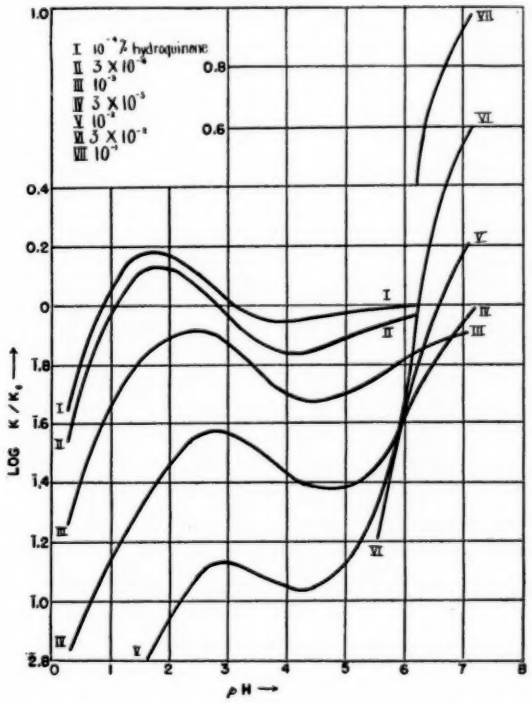

FIG. 4. Effect of hydroquinone on oxidation rate.

The author is indebted to Professor E. K. Rideal for much helpful advice and criticism, and to Imperial Chemical Industries (Dyestuffs Group) for financial aid.

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Photochemical Studies. XXV. The Direct Photochemical Decomposition of Nitrous Oxide

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The number of molecules of gas uncondensed by liquid air formed per quantum absorbed by nitrous oxide has been determined both in the presence and absence of mercury. At least part of the primary dissociation must be into nitrogen molecules and oxygen atoms. A mechanism consistent with the facts involves the subsequent reactions $O+N_2O=2NO$ and $O+O=O_2$. However, it is impossible to state definitely that none of the primary dissociation is into nitric oxide molecules and nitrogen atoms. The weakness of the absorption suggests that the absorption is "forbidden" and it is possible that the nitrogen molecules and oxygen atoms are produced in their normal electronic states (with perhaps some vibrational energy in the nitrogen molecule).

THE photochemical decomposition of nitrous oxide presents a real theoretical interest because the number of possible modes of primary dissociation is limited to two and because the number of secondary reactions cannot be large. A study of the decomposition sensitized by mercury vapor was recently published,[1] but it

[1] Manning and Noyes, J. Am. Chem. Soc. **54**, 3907 (1932).

proved impossible to present conclusive evidence in favor of either primary step, although the initial production of a nitrogen molecule and of an oxygen atom afforded a somewhat better explanation of the experimental facts than did a dissociation into a molecule of nitric oxide and a nitrogen atom.

The spectrum of nitrous oxide has been studied by many investigators.[2] Due to the limited number of modes of dissociation and the well-known energy levels of the possible dissociation products, the temptation has been great to associate long wave limits of various absorption regions with energies corresponding to definite modes of dissociation. That most of the agreements obtained were fortuitous will be made evident in the following paragraphs. For this molecule, as well as for many others, this line of evidence gives no definite indication of the nature of the dissociation products. Changes in the heats of dissociation of nitrogen and oxygen have destroyed even the apparent agreement which existed in the past.

The absorption spectrum of nitrous oxide between 1800 and 2000A is apparently perfectly continuous.[2] Only frequencies corresponding to modes of vibration in which the atoms are displaced along the axis of symmetry would be totally symmetrical, since the molecule is linear and nonsymmetrical (NNO).[3] These frequencies are all relatively large in the ground state and while they would doubtless be modified in upper electronic levels, the separation between vibration levels should be sufficient to permit any vibrational structure in the absorption to be detected. If the molecule is not linear in the upper state, the appearance of the spectrum could not at present be predicted, but the absence of bands even at relatively high pressures and long path length[4, 1] would indicate strongly that the upper electron state involved in this absorption region is repulsive.

An aluminum spark in air was used as a source of illumination, giving wave-length greater than 1850A, corresponding to about 6.7 electron volts or less. However, the absorption extends to at least 2300A,[4] equivalent to about 5.4 electron volts. Energetically the following primary dissociations are the only ones which need to be considered[5]

$$N_2O = N_2(^1\Sigma) + O(^3P); \quad \Delta E \leqq 1.81 \text{ ev}; \quad \lambda < 6800\text{A}, \quad (1)$$

$$N_2O = N_2(^1\Sigma) + O(^1D); \quad \Delta E \leqq 3.71 \text{ ev}; \quad \lambda < 3300\text{A}, \quad (2)$$

$$N_2O = NO(^2\Pi) + N(^4S); \quad \Delta E \leqq 3.87 \text{ ev}; \quad \lambda < 3190\text{A}. \quad (3)$$

Electronic excitation of the N_2 and NO molecules would be impossible, although they might be formed with a certain amount of vibrational energy.

Only one determination of the quantum yield of photochemical decomposition of nitrous oxide seems to have been made.[6] The reaction was found to follow the equation

$$4N_2O = 3N_2 + 2NO + O_2 \quad (4)$$

and the value reported for the quantum yield was four. The author could only explain this large value by assuming the initial production of excited molecules, but as shown above this is unlikely in view of the type of absorption spectrum. Following a primary dissociation, secondary reactions would seem to afford a maximum quantum yield of two unless one postulates a very improbable energy chain mechanism.

It is perhaps significant that it is possible to explain the formation of oxygen only if (1) or (2) takes place, unless a secondary reaction between nitrogen atoms and nitric oxide is responsible.[1]

Experimental

The number of molecules of nitrous oxide decomposing per quantum absorbed was not deter-

[2] See Duncan, J. Chem. Phys. **4**, 638 (1936) for a study of the far ultraviolet spectrum of nitrous oxide. This article as well as reference 1 contain references to most of the work on the spectrum of this molecule.

[3] Plyler and Barker, Phys. Rev. **38**, 1827 (1931); Bailey and Cassie, ibid. **39**, 534 (1932).

[4] Wulf and Melvin, Phys. Rev. **39**, 180 (1932).

[5] The dissociation energies of N_2 and O_2 are taken as 7.34 and 5.09 ev, respectively (Mulliken, Phys. Rev. **46**, 144 (1934) and Herzberg, Zeits. f. physik. Chemie **B10**, 189 (1930)). The heats of formation of N_2O (Ramsperger and Waddington, Proc. Nat. Acad. Sci. **17**, 104 (1931)) and NO (Lewis and Randall, *Thermodynamics* (McGraw-Hill Book Co., Inc., New York, 1923), p. 560) correspond to 0.74 and 0.94 ev, respectively. The $2p^4\,{}^1S$ state of O and the $2p^3\,{}^2D$ and $2p^3\,{}^2P$ states of N may be of importance if more than one type of dissociation (beginning below 2000A) needs to be considered.

[6] Macdonald, J. Chem. Soc. 1 (1928).

mined directly. Instead the number of molecules of gas uncondensed by liquid air produced from nitrous oxide per quantum absorbed was determined. This was done (a) with mercury vapor present and (b) in a system as free as possible from mercury vapor and all substances which might react with the products of the reaction.

(a) Radiation from an aluminum spark was focused by a quartz lens through a diaphragm onto the back window of a fused quartz cell. Back of the quartz cell and attached to it by Royal Scarlet sealing wax was the actinometer, in which hydrogen bromide was used as the standard substance. The sealing wax was about 11 cm from the illuminated zone and the area exposed was kept small. The actinometer was separated from the McLeod gauge and vacuum line by a trap always immersed in dry ice and ether to prevent mercurous bromide from depositing rapidly on the window of the reaction vessel.

One molecule of hydrogen, uncondensed by liquid air, is assumed to be formed from hydrogen bromide per quantum absorbed. Pressures of 3–6 cm of hydrogen bromide were used, the absorption of the active radiation being practically complete under these conditions.[7]

The thermal decomposition of the hydrogen bromide could not be neglected, so that the amount of decomposition for a given time of illumination with the nitrous oxide uncondensed by liquid air was subtracted from the amount obtained during exactly the same time with the nitrous oxide frozen down. In case of variations in intensity (as determined by a thermopile) a connection based on the amount of hydrogen bromide decomposing in the same time interval without illumination was made. These connections were small.

The effective volumes of both systems were determined after each run by measuring the pressures on McLeod gauges and then evacuating both lines to negligibles pressures. The gases trapped in the gauges were released and the pressures read again. The effective volumes of the systems could be calculated from the ratio of pressures and the known volumes of the McLeod gauges.

The transmission of the window between the reaction cell and the actinometer was also of importance. This was obtained by filling both cells with hydrogen bromide. The relative amounts of hydrogen produced in the two cells with the same intensity of illumination could be used to obtain a factor correcting not only for the transmission of the window but the volume of the reaction system.

Following illumination liquid air was placed on a trap and the pressure measured. This was repeated at frequent intervals for several days until the pressure became constant. During this time the pressure increased 1.5 to 2.0 times that read immediately after illumination. This behavior seems to be typical of systems containing nitric oxide, mercury and oxygen.[8]

The following sample calculation shows how the data were treated: (1) From data obtained when both lines were filled with HBr one finds:

$$\frac{\text{No. quanta absorbed } N_2O \text{ line}}{\text{No. quanta absorbed HBr line}} = (1.86 \pm 0.03)\, FV_1 \times 10^2,$$

where F is the factor of the McLeod gauge used in the N_2O line and V_1 is its volume. (2) Pressure of products = 19.87 arbitrary units at 25°C.

$$\frac{\text{Volume of line}}{\text{Volume of gauge}} = 3.71.$$

No. molecules $= 19.87 \times 3.71 \times 3.259 \times 10^{17}\ FV_1$, where 3.259×10^{17} = no. molecules per cc at 1 mm pressure at 25°C. Pressure of H_2 produced from HBr (N_2O frozen down) − pressure of H_2 produced from HB_2 (N_2O not frozen down) = 0.275 arbitrary units. No. quanta $= 0.275 \times 2.570 \times 10^{17} \times 1.86 \times 10^2\ FV_1$, where 2.570×10^{17} = no. molecules in HBr line at 25°C when pressure is 1 arbitrary unit.

Therefore quantum yield

$$= \frac{M}{N} = \frac{19.87 \times 3.71 \times 3.259 \times 10^{17} FV_1}{0.275 \times 2.570 \times 1.86 \times 10^{19} FV_1}$$

$$= 1.8_2.$$

The preparation and purification of the nitrous oxide and hydrogen bromide have ben described.[1, 7]

[7] Howe and Noyes, J. Am. Chem. Soc. **58**, 1404 (1936).

[8] Noyes, J. Am. Chem. Soc. **53**, 514 (1931); Flory and Johnston, ibid., **57**, 2641 (1935).

Table I shows the results obtained with the technique just described.

TABLE I. *Quantum yield of gas formation from nitrous oxide with mercury present.*

PRESSURE N_2O CM	NO. MOLECULES UNCONDENSED BY LIQUID AIR FORMED PER QUANTUM ABSORBED	INTENSITY (ARBITRARY UNITS)
18.5	2.1_4	2.5
18.3	2.3_9	3.4
18.2	1.9_1	3.1
8.3	2.0_0	5.5
4.9	2.6_2	2.6
4.7	1.6_2	4.2
3.5	2.1_7	3.9
3.5	1.8_6	3.4
1.4	1.9_8	5.2
1.35	1.5_7	4.8
1.2	1.8_3	2.8
1.2	1.3_0	5.2
	Av. 1.9_5	

Nineteen additional runs were made in which the reaction products were not always pumped out between runs. These agree somewhat less well among themselves than the runs in Table I. As a weighted mean of all results we may take 1.9 ± 0.2. There seems to be no significant variation of yield either with total pressure or with intensity. There is, perhaps, a slight tendency for the yield to decrease at low pressures, but the values are somewhat less reliable under these conditions due to the small absorption by the N_2O.

(b) Experiments in the absence of mercury vapor were carried out in a system from which mercury vapor was excluded from the beginning of the preparation of the line by a trap immersed in liquid air. Nitrous oxide was prepared as before and part condensed into the reaction line while the rest was allowed to escape through the diffusion pump. The line was then closed off by a stopcock and the pressure of N_2O read on an Apiezon oil manometer. At all times the stopcock and Apiezon oil manometer were separated from the line to be used subsequently by a trap immersed in dry ice and ether. The nitrous oxide was then condensed in the reaction line and the vessel and pressure gauge sealed off. Pressures of the gases uncondensed by liquid air were read by a quartz fiber gauge which had been calibrated using air. Since the only gases measured were NO (M.W. = 30), O_2 (M.W. = 32) and N_2 (M.W. = 28) the use of air (average M.W. = 29) in calibrating the gauge introduced errors not exceeding 5 percent which would be small compared to other errors in these experiments. The number of quanta absorbed by the nitrous oxide was obtained as before and the transmission of the window between the reaction vessel and the actinometer again obtained by filling both systems with hydrogen bromide and adding a McLeod gauge to the nitrous oxide line. The volume of the N_2O line was obtained by filling the various parts of the line from a burette after they had been taken part.

The calculations in this case were made by obtaining the pressure of hydrogen in the hydrogen bromide line both when the nitrous oxide was frozen down with liquid air and when it was not. Since one molecule of H_2 is formed per quantum absorbed, the number of quanta absorbed by the N_2O could be calculated by dividing the difference in the numbers of molecules of hydrogen produced under the two conditions by the transmission of the window. The number of molecules produced by decomposition of the N_2O which were uncondensed by liquid air, was calculated from the pressure and volume of the system, due account being taken of the part of the line which was at the temperature of the liquid air.

For most of these runs the group of aluminum lines between 1860 and 1990A was separated by focal isolation. This reduced the intensity, thereby introducing larger errors due to variations in the rate of thermal decomposition of the hydrogen bromide. This is probably the main reason for the less satisfactory concordance of the results in these experiments.

During the first runs made the same increase in pressure after illumination was noted as before. However, with greater precautions to eliminate mercury vapor and the introduction of the dry ice ether trap to reduce the amount of impurity from the Apiezon oil and the stopcock grease, this effect disappeared.

Two runs were made at the end without mercury vapor but with the Apiezon oil manometer still attached. No attempt was made to make quantum yield measurements under these conditions, but enough decomposition was obtained so that the increase in total pressure during exposure could be compared with the

pressure of gas uncondensed by liquid air. The results were not very satisfactory (due partially to the solubility of N_2O in the Apiezon oil), but it is interesting to note that after freezing the gases with liquid air and allowing them to evaporate, but not before, the color of NO_2 could be observed in the line. This proves that NO and O_2 are both formed during illumination, as observed by Macdonald.[6]

Table II presents the data obtained in the absence of mercury vapor.

Discussion of Results

Since NO_2 is formed in the liquid-air trap, both oxygen and nitric oxide must be formed during irradiation. The pressure increase upon standing after illumination is observed also in a system of nitric oxide which has been irradiated when mercury is present.[8]

In view of what is known about the behavior of mercury and nitrogen dioxide it is possible to show that either reaction (1) or reaction (2) followed by (5)–(9) will account for the observed facts. It is not possible to show that (3) does not take place at all.

$$O+N_2O=2NO, \tag{5}$$

$$O+O+M=O_2+M, \tag{6}$$

$$NO+\tfrac{1}{2}O_2=NO_2, \tag{7}$$

$$Hg+NO_2=HgNO_2, \tag{8}$$

$$HgNO_2=HgO+NO. \tag{9}$$

If mercury is not present NO_2 will be removed by the liquid-air trap and (8) and (9) will not take place. If NO is formed in excess of that required to react with all of the oxygen by Eq. (7), we may write

$$N_1=N_2+\tfrac{1}{2}N_3=2N_4+N_3, \tag{10}$$

where N_1=no. molecules N_2O disappearing, N_2=no. molecules nitrogen formed, N_3=no. molecules nitric oxide formed, N_4=no. molecules oxygen formed, all per quantum absorbed. But

$$N_2=1 \tag{11}$$

and experimentally in the presence of mercury

$$N_2+N_3=1.90=1+N_3=\phi_1, \tag{12}$$

$$N_3=0.90. \tag{13}$$

Therefore from Eq. (10)

$$1+0.45=2N_4+0.90; \quad N_4=0.275. \tag{14}$$

Since $N_3>2\,N_4$, the number of molecules of oxygen will determine the amount of NO_2 condensed in the liquid-air trap in the absence of mercury. Therefore the number of molecules measured in the gas phase per quantum absorbed will be

$$\phi_2=N_2+N_3+N_4-3N_4 \tag{15}$$

$$=1+0.90+0.275-0.825$$

$$=1.35. \tag{16}$$

This is in satisfactory agreement with the value given in Table II and shows that the data are not inconsistent with the mechanism.

However, it is possible to satisfy the results by assuming both types of primary process, Eqs. (17)–(20).

$$N_2O+h\nu=N_2+O, \tag{17}$$

$$O+O=O_2, \tag{18}$$

$$N_2O+h\nu=NO+N, \tag{19}$$

$$N+N_2O=NO+N_2. \tag{20}$$

If the two primary processes are equally probable, the quantum yields would be 1.75 and 1.25 respectively in the presence and in the absence of mercury. However, the occurrence of reaction (5) is rendered probable by studies on the thermal decomposition of N_2O.[9] This combined with evidence from the sensitized decomposition[1] indicates strongly that either (1) or (2) and (5)–(9) represent the mechanism of the decomposition. It can be said with certainty that (3) cannot be the sole primary step.

It is of interest to give the apparent over-all reaction under the experimental conditions used.

Table II. *Quantum yield of gas formation from nitrous oxide with mercury absent.*

Pressure N_2O cm	No. Molecules Uncondensed by Liquid Air per Quantum Absorbed	Av. Intensity [a] (Arbitrary Units)	No. Observation
11	1.4_5	4.5	5
6.9	1.2_5	3.9	9
	Av. 1.3 ± 0.2		

[a] The arbitrary units are not the same as in Table I.

[9] Musgrave and Hinshelwood, Proc. Roy. Soc. **A135**, 23 (1932).

This is

$$4N_2O = 2.8N_2 + 2.5NO + 0.7O_2, \qquad (21)$$

which may be compared with Eq. (4) obtained by Macdonald.

It should be noted that the formation of O_2 from oxygen atoms should proceed either as a three-body process or on the walls. Experimental conditions may be expected to influence the ratio of nitric oxide to oxygen, although it is usually difficult to find exact agreement with a rate expression based upon homogeneous gas phase association of atoms. At low intensities this ratio would probably not vary greatly, while a low pressure of nitrous oxide would tend to cause an increase in the amount of oxygen and a decrease in the quantum yield. The data in Table I show a trend such as this, but measurements could not be extended to very low pressures because of the low absorption coefficient of nitrous oxide.

Some further speculations concerning the primary process may be made. Herzberg[10] has given reasons for believing that a normal N_2O molecule would separate adiabatically according to Eq. (2). Since N_2O in its normal state is linear, diamagnetic and possesses a small dipole moment, it is doubtless $^1\Sigma^+$, with an electron structure somewhat similar to CO_2. The absorption region with which we are concerned is extremely weak, at least compared to those at shorter wave-lengths.[2] It is possible, therefore, that the transition is "forbidden."

If an oxygen atom (or a nitrogen atom) is made to approach a nonrotating nitrogen molecule (or nitric oxide molecule) end-on, the states of the resulting N_2O molecule may be predicted. However if the fragments as they separate depart from linearity, these predictions have no bearing on the present case except as regards multiplicity.

[10] Herzberg, Zeits. f. physik. Chemie **B17**, 68 (1932).

The predicted states are as follows:

(a) From $O(^3P) + N_2(^1\Sigma_g^+)$: $^3\Sigma^-$, $^3\Pi$,

(b) From $O(^1D) + N_2(^1\Sigma_g^+)$: $^1\Sigma^+$, $^1\Pi$, $^1\Delta$,

(c) From $N(^4S) + NO(^2\Pi)$: $^3\Pi$, $^5\Pi$.

Singlet→triplet transitions should be weak, as for diamagnetic molecules, and $\Sigma \rightarrow \Pi$ transitions should be relatively weak. The upper state[11] may be $^1\Pi$ or $^3\Pi$ (although $^3\Sigma$ is not entirely excluded as a possibility). The former could give reaction (2) and the latter either reaction (1) or (3). Since for photochemical reasons either reaction (1) or (2) must take place to a large extent, theory does not predict definitely whether the oxygen atoms will be ^3P or ^1D. The weakness of the absorption is supporting evidence for a $^3\Pi$ upper state, in which case the oxygen atoms would be produced in their normal (^3P) states.

The transparency of N_2O in the visible and near ultraviolet must be due: (1) to the "forbidden" character of the transition; (2) to considerations based on an application of the Franck-Condon principle.

The interaction between the upper (repulsive) state and the ground state of N_2O must be weak, although the failure of attempts[12] to synthesize N_2O from ^1D oxygen atoms and normal nitrogen molecules would seem to indicate a large amount of such interaction. However, one might expect the "steric" factor for such a reaction to be very small.

The absence of a banded spectrum in N_2O even at high pressures and at long path lengths indicates that the upper state is repulsive and it seems probable that the products are formed in their ground states with large amounts of kinetic energy.

[11] Cf. Mulliken, J. Chem. Phys. **3**, 736 (1935).

[12] A. B. Steiner, Ph.D. Thesis, Stanford University, 1937; kindly communicated by Professor P. A. Leighton.

Bond Force Constants and Vibrational Frequencies of Some Hydrocarbons[1]

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By use of valence forces, the normal coordinate method of treating vibrations has been applied to a number of related molecules and twenty-nine frequencies have been calculated and compared with experiment. The molecules considered are methylacetylene, dimethylacetylene, acetylene, diacetylene, ethane and methane. The frequencies calculated include all of the nondegenerate frequencies for the above molecules and the degenerate frequencies of methane. A set of five force constants has been applied to all of the molecules with fairly good results. The calculations have been carried out for both liquids and gases, a slightly different set of force constants being assigned to each state of aggregation.

I. INTRODUCTION

IN this paper there will be given calculations for the vibrational frequencies of a number of hydrocarbons. Originally the calculations were started only for methylacetylene and dimethylacetylene in order to interpret the experimental results obtained by us for those substances.[2] However, it was felt desirable to extend the calculations to include a number of related molecules in order to demonstrate that bond force constants could be used interchangeably in most cases for molecules containing similar bonds. Moreover the calculations have been carried out separately for liquids and for gases with a view toward establishing a set of force constants for each state of aggregation. Although assigning different sets of force constants to molecules in different states appears to be an arbitrary way of taking care of the intermolecular forces which are large for liquids, it is believed that the results are sufficiently good to warrant that procedure. The complete list of molecules is methylacetylene ($CH_3C\equiv CH$), dimethylacetylene ($CH_3C\equiv CCH_3$), acetylene ($HC\equiv CH$), diacetylene ($HC\equiv C-C\equiv CH$), ethane (CH_3CH_3) and methane (CH_4). Of these molecules, the last four have been treated by other authors[3] but they are also included here for reasons given above.

Except for methane only the nondegenerate frequencies will be considered. For the molecules with threefold symmetry axes, only the vibrations symmetric with respect to those axes are nondegenerate, and for the linear molecules only the valence type vibrations are nondegenerate. Methane has four frequencies all of which are here considered. They include a totally symmetric nondegenerate frequency, one doubly degenerate frequency and two triply degenerate frequencies. In Table I is shown a list of the molecules with the number of vibrations of the various types. The numbers followed by *s* refer to symmetric vibrations, whereas those followed by *a* refer to antisymmetric vibrations. The figures for dimethylacetylene and ethane are exclusive of the vibrations corresponding to rotation of the methyl groups with respect to each other. For dimethylacetylene the rotation

TABLE I. *Molecules considered.*

FORMULA	NUMBER OF VIBRATIONS NONDEGENERATE	DEGENERATE
$CH_3C\equiv CH$	5	5
$CH_3C\equiv CCH_3$	4*s* 3*a*	8
$HC\equiv CH$	2*s* 1*a*	2
$HC\equiv C-C\equiv CH$	3*s* 2*a*	4
CH_3CH_3	3*s* 2*a*	6
CH_4	1	1, 2
	26	
Degenerate frequencies of Methane	3	
Total	29	

[1] This article is based upon part of a thesis presented to the Graduate School of the University of Minnesota by F. T. Wall in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1937.

[2] Glockler and Davis, J. Chem. Phys. **2**, 881 (1934); Glockler and Wall, Phys. Rev. **51**, 529 (1937).

[3] Acetylene: Mecke, Zeits. f. Physik **64**, 173 (1930); Olson and Kramers, J. Am. Chem. Soc., **54**, 136 (1932). Diacetylene: Bartholomé, Zeits. f. physik. Chemie **B23**, 152 (1933). Ethane: Sutherland and Dennison, Proc. Roy. Soc. **A148**, 250 (1935); Howard, J. Chem. Phys. **5**, 442 (1937). Methane: Dennison and Johnston, Phys. Rev. **47**, 93 (1935).

must be nearly free because the methyl groups are so far apart, but for ethane the rotation may be retarded.[4]

Five Hooke's law force constants are identified as shown in Table II. It will be assumed in subsequent calculations that the constants have the same values for all of the molecules in which the corresponding bond type occurs. It is further assumed that the bending constants for the H−C−H angles and the H−C−C angles are the same. It will be noted that there appears a term r^2_{C-H} in the expression for the potential energy arising from bending an angle. The term r^2_{C-H} is introduced to make k_3 dimensionally the same as the other force constants. Moreover it turns out that k_3 as indicated in the table and not $k_3 r^2_{C-H}$ is what can be determined experimentally from vibrational frequencies alone. It is of interest to note that although the five force constants are sufficient in setting up potential energy functions for all of the twenty-nine frequencies here considered, all five are also necessary for methylacetylene alone. From the standpoint of variety of bonds and low symmetry, methylacetylene is the most complicated of the molecules listed in Table I.

II. The Secular Equation of Methylacetylene

Because the nondegenerate frequencies of methylacetylene are symmetric with respect to the threefold axis of the molecule, it is sufficient for a dynamical consideration of the problem to take one hydrogen of the three methyl hydrogens as representative of all three. Indicating methylacetylene by the diagram of Fig. 1, the hydrogen marked "1" is taken as the representative hydrogen. The kinetic and potential energies will be given by

$$T=\tfrac{3}{2}m_1(\dot{x}_1^2+\dot{y}_1^2)+\tfrac{1}{2}m_2(\dot{x}_2^2+\dot{x}_3^2+\dot{x}_4^2)+\tfrac{1}{2}m_1\dot{x}_5^2$$

$$V=\tfrac{3}{2}k_1\xi_{12}^2+\tfrac{1}{2}k_2\xi_{23}^2+2\tfrac{3}{2}k_3 r_{12}^2\eta^2+\tfrac{1}{2}k_4\xi_{34}^2+\tfrac{1}{2}k_5\xi_{45}^2,$$

$\xi_{ij}=r_{ij}-r^\circ_{ij}$, $\eta=\theta-\theta^\circ$,
m_1 = mass of hydrogen atom,
m_2 = mass of carbon atom.

The first term in the kinetic energy expression has a coefficient $\frac{3}{2}$ instead of $\frac{1}{2}$ because there are three hydrogens behaving similarly. Likewise the factor $\frac{3}{2}$ appears in the first and third terms of the potential energy expression. The factor 2 is introduced into the third term of the potential energy because there are two angles changing for each hydrogen. The two angles are ϕ and θ as indicated in Fig. 1. They are respectively the H−C−H angles and the supplements to the H−C−C angles. It will be assumed that at equilibrium the angles are tetrahedral. In addition to being a plausible assumption, it has the advantage of making the last mentioned factor exactly 2 instead of some less convenient number. For tetrahedral equilibrium angles a small change in θ is accompanied by an *equal* small change in ϕ for the nondegenerate vibrations.

If the x's and y_1 represent small displacements from equilibrium positions, there will exist linear relationships between them and the ξ's and η. It is then possible to set up equations of motion in terms of the ξ's and η and by the usual methods arrive at a secular equation. The secular equation for methylacetylene is as follows:

$$\begin{vmatrix} \lambda+A & B & C & 0 & 0 \\ D & \lambda+E & F & 0 & 0 \\ G & -3B & \lambda-6C & H & 0 \\ 0 & 0 & 3C & \lambda-2H & I \\ 0 & 0 & 0 & H & \lambda+J \end{vmatrix}=0,$$

$\lambda=4\pi^2\nu^2$, ν = vibrational frequency,

$$A=-k_1\left(\frac{1}{3m_2}+\frac{1}{m_1}\right) \qquad F=-\frac{(8)^{\frac{1}{2}}k_2}{3m_2 r_{12}},$$

$$B=\frac{2(8)^{\frac{1}{2}}k_3 r_{12}}{3m_2}, \qquad G=\frac{k_1}{m_2},$$

$$C=\frac{k_2}{3m_2}, \qquad H=\frac{k_4}{m_2},$$

$$D=\frac{(8)^{\frac{1}{2}}k_1}{3m_2 r_{12}}, \qquad I=\frac{k_5}{m_2},$$

$$E=-2k_3\left(\frac{8}{3m_2}+\frac{1}{m_1}\right), \qquad J=-k_5\left(\frac{1}{m_2}+\frac{1}{m_1}\right).$$

The roots of the above secular equation will give the vibrational frequencies of methylacetylene. Before expanding that equation and work-

[4] Howard, J. Chem Phys. 5, 442 (1937).

ing with it numerically, the equations for some other molecules will be considered.

III. The Secular Equations of Acetylene, Ethane, Dimethylacetylene and Diacetylene

By methods similar to those employed for methylacetylene, the secular equations for acetylene and ethane can readily be derived. The equation for acetylene is

$$\begin{vmatrix} \lambda+J & H & 0 \\ I & \lambda-2H & I \\ 0 & H & \lambda+J \end{vmatrix} = 0.$$

For ethane the equation is

$$\begin{vmatrix} \lambda+A & B & C & 0 & 0 \\ D & \lambda+E & F & 0 & 0 \\ G & -3B & \lambda-6C & -3B & G \\ 0 & 0 & F & \lambda+E & D \\ 0 & 0 & C & B & \lambda+A \end{vmatrix} = 0.$$

Examination of the secular equations for methylacetylene, acetylene and ethane will reveal the following remarkable fact. The methylacetylene equation down to the term $\lambda-6C$ is precisely the same as the ethane equation down to the same term. Also the lower right-hand corner of the methylacetylene equation is like the corresponding corner of the acetylene equation. Thus because one end of methylacetylene ($CH_3C{\equiv}CH$) is like one end of ethane (CH_3CH_3) and the other end is like an end of acetylene ($HC{\equiv}CH$), the ends of the secular equations are related. The molecular structure of a molecule is accordingly related to its determinantal equation.

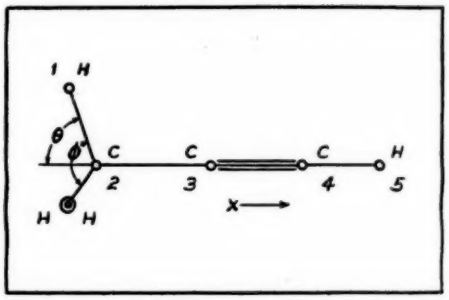

Fig. 1. Methylacetylene.

It will be further noted that the equations for ethane and acetylene are symmetrical about their middle terms whereas the equation for methylacetylene has no such symmetry. It is apparent that the symmetry or lack of symmetry will show up in the secular equations. By inspection of the equations so far written down, it is easily seen what the equation for dimethylacetylene will be. It will be like the methylacetylene equation down to the term $\lambda-2H$ and in addition will be symmetrical about that term. The equation for dimethylacetylene is as follow:

$$\begin{vmatrix} \lambda+A & B & C & 0 & 0 & 0 & 0 \\ D & \lambda+E & F & 0 & 0 & 0 & 0 \\ G & -3B & \lambda-6C & H & 0 & 0 & 0 \\ 0 & 0 & 3C & \lambda-2H & 3C & 0 & 0 \\ 0 & 0 & 0 & H & \lambda-6C & -3B & G \\ 0 & 0 & 0 & 0 & F & \lambda+E & D \\ 0 & 0 & 0 & 0 & C & B & \lambda+A \end{vmatrix} = 0.$$

By actually carrying out the detailed work, the above equation can be derived. Similarly the equation for diacetylene can be written down. It will be related to the acetylene end of methylacetylene but will be symmetrical about the carbon−carbon single bond (C−C) term, namely: $\lambda-6C$. Secular equation for diacetylene:

$$\begin{vmatrix} \lambda+J & H & 0 & 0 & 0 \\ I & \lambda-2H & 3C & 0 & 0 \\ 0 & H & \lambda-6C & H & 0 \\ 0 & 0 & 3C & \lambda-2H & I \\ 0 & 0 & 0 & H & \lambda+J \end{vmatrix} = 0.$$

Table II.

Constant	Bond Type	Potential Energy
k_1	H−C of methyl etc.	$V=\frac{1}{2}k_1(\Delta r_{C-H})^2$
k_2	C−C of ethane etc.	$V=\frac{1}{2}k_2(\Delta r_{C-C})^2$
k_3	H or H C−H C−C of methane, ethane etc.	$V=\frac{1}{2}k_3 r^2_{C-H}(\Delta\theta)^2$
k_4	C≡C of acetylene etc.	$V=\frac{1}{2}k_4(\Delta r_{C\equiv C})^2$
k_5	≡C−H of acetylene etc.	$V=\frac{1}{2}k_5(\Delta r_{\equiv C-H})^2$

The equations for methane cannot be simply related to those already shown. Methane is best treated as an individual but the derivations will not be given here since it has already been given in the literature.[3]

IV. Expanded Equations

Because of their symmetrical nature, the secular equations given in the preceding section can each be separated into two factors. One of them for each of the equations will be of a degree *one* greater than the other factor. The roots of the factor with the higher degree will correspond to *symmetric* vibrations whereas the others correspond to *antisymmetric* vibrations. Since the equation for methylacetylene is not symmetrical, it will not factor, and its vibrations cannot be subdivided into classes according to symmetry properties.

Letting $k_1'=-A$, $k_2'=6C$, $k_3'=-E$, $k_4'=2H$, $k_5'=-J$, $m_1=1$, and $m_2=12$,

the equations have been factored whenever possible and then expanded to give the following:
Methylacetylene:

$$\lambda^5-A'\lambda^4+B'\lambda^3-C'\lambda^2+D'\lambda-E'=0,$$

where

$$A'=k_1'+k_2'+k_3'+k_4'+k_5',$$

$$B'=405/407k_1'k_3'+73/74k_1'k_2'+k_1'k_4'+k_1'k_5'+10/11k_2'k_3'+k_3'k_4'+k_3'k_5'+3/4k_2'k_4'+k_2'k_5'+25/26k_4'k_5',$$

$$C'=729/814k_1'k_2'k_3'+405/407k_1'k_3'k_4'+405/407k_1'k_3'k_5'+109/148k_1'k_2'k_4'+73/74k_1'k_2'k_5'+25/26k_1'k_4'k_5'+29/44k_2'k_3'k_4'+10/11k_2'k_3'k_5'+25/26k_3'k_4'k_5'+37/52k_2'k_4'k_5',$$

$$D'=1053/1628k_1'k_2'k_3'k_4'+729/814k_1'k_2'k_3'k_5'+336/481k_1'k_2'k_4'k_5'+10125/10582k_1'k_3'k_4'k_5'+357/572k_2'k_3'k_4'k_5',$$

$$E'=3240/5291k_1'k_2'k_3'k_4'k_5'.$$

Dimethylacetylene (symmetric factor):

$$\lambda^4-(k_1'+k_2'+k_3'+k_4')\lambda^3+(73/74k_1'k_2'+405/407k_1'k_3'+k_1'k_4'+10/11k_2'k_3'+1/2k_2'k_4'+k_3'k_4')\lambda^2-(729/814k_1'k_2'k_3'+18/37k_1'k_2'k_4'+405/407k_1'k_3'k_4'+9/22k_2'k_3'k_4')\lambda+162/405k_1'k_2'k_3'k_4'=0.$$

Acetylene (symmetric equation):

$$\lambda^2-(k_4'+k_5')\lambda+12/13k_4'k_5'=0.$$

Diacetylene (symmetric factor):

$$\lambda^3-(k_2'+k_4'+k_5')\lambda^2+(1/2k_2'k_4'+k_2'k_5'+25/26k_4'k_5')\lambda-6/13k_2'k_4'k_5'=0.$$

Ethane (symmetric factor):

$$\lambda^3-(k_1'+k_2'+k_3')\lambda^2+(36/37k_1'k_2'+405/407k_1'k_3'+9/11k_2'k_3')\lambda-324/407\,k_1'k_2'k_3'=0.$$

Methane:

$\lambda=k_1$ (nondegenerate),
$\lambda=3k_0$ (doubly degenerate),
$\lambda^2-(10/9k_1+22/9k_3)\lambda+8/3k_1k_3=0$ (triply degenerate).

The equations for the antisymmetric frequencies of dimethylacetylene, acetylene, diacetylene and ethane can be obtained from the corresponding symmetric equations by setting the force constant for the central bond of the molecule equal to zero wherever it appears in the symmetric equation.

V. Numerical Calculations; Discussion

The numerical calculations have been carried out for both liquids and gases using different sets of force constants. For convenience of numerical work λ was taken to be 10^{-6} times the square of the frequency in wave numbers (cm^{-1}). Taking five frequencies to adjust the force constants, the other twenty-four frequencies have been calculated. The values of the force constants obtained by using the equations of the preceding section in the manner just indicated will not be in dynes per centimeter. To convert the values to dynes per centimeter it is necessary to multiply the k's (unprimed) by

$$\frac{4\pi^2c^2\times10^6}{N}=5.86\times10^4,$$

c = velocity of light,
N = Avogadro's number.

TABLE III.

MOLECULE	FREQUENCY TYPE		GASES CALC. cm^{-1}	GASES OBS. cm^{-1}	LIQUIDS Calc. cm^{-1}	LIQUIDS Obs. cm^{-1}
$CH_3C\equiv CH$	C−C		(930)	930	(929.5)	929.5
	H, C−C		1403		(1382.5)	1382.5
	C≡C		2188	2142	2177.6	2123.5
	H−C (methyl)		2908	2911††	(2896.6)	2896.6†
	≡C−H		3337		3301	3305
$CH_3C\equiv CCH_3$	C−C	*a*	1103		1100	
	H, C−C	*a*	1504		1492	
	H−C	*a*	2908		2896	
	C−C	*s*	725		726	697;774
	H, C−C	*s*	1373		1349	1379
	C≡C	*s*	2343		2334	2274†
	H−C	*s*	2909	2909††	2897	2891†
$HC\equiv CH$	≡C−H	*a*	3294	3277	3258	
	C≡C	*s*	(1974)	1974	(1959)	1959
	≡C−H	*s*	(3374)	3374	(3338)	3338
$HC\equiv C-C\equiv CH$	C≡C	*a*	2038	2085	2023	
	≡C−H	*a*	3336	3350	3300	
	C−C	*s*	823		826	644
	C≡C	*s*	2289		2281	2183
	≡C−H	*s*	3339		3303	
CH_3CH_3	H, C−C	*a*	1315	1380	1288	
	H−C	*a*	2902	2926†	2890	
	C−C	*s*	1000	993	994	990
	H, C−C	*s*	1563		1554	1460
	H−C	*s*	2914	2927†	2902	2920†
CH_4	H, C−H	*d*	(1304)	1304	1277	
	H, C−H	*d*	1461		1431	
	H−C	*s*	2861	2915	2849	2909
	H−C	*d*	(3022)	3022	3009	2999

The calculated results with comparisons to experimental values are given in Table III. The numbers in parentheses were used to adjust force constants. Under the column headed "Frequency Type" there are given whenever possible symmetry designations and the bonds principally involved in the vibrations. The experimental values are taken from Raman and infrared work.[2, 5] Since the infrared work has been done only for gases, no comparisons are possible for the antisymmetric liquid frequencies because the antisymmetric frequencies are forbidden in the Raman effect. Other gaps will also be found in the table because of incomplete results.

The experimental values followed by a dagger (†) are the means of two observed frequencies arising because of resonance associated with accidental degeneracy.[6] For gaseous methyl and dimethylacetylenes only one C−H frequency was observed for each,[2] but it is believed that better experimental conditions would have yielded two, the second frequency having a lower value in each case. This is an analogy to the liquid cases, where two lines were observed, the higher of which had the much greater intensity. Assuming that the doublet separations for the C−H frequencies is the same for the gases as for the liquids, "mean values" have been calculated for the gases. In the table these values are followed by two daggers (††).

[5] See Hibben, Chem. Rev. **18**, 1 (1936) and Stuart, *Molekulstruktur* (J. Springer, Berlin, 1934) for other references.

TABLE IV. *Values of force constants.*

CONSTANT	BOND TYPE	k DYNES/CM Gases	k DYNES/CM Liquids
k_1	C−H	4.795×10^5	4.756×10^5
k_2	C−C	6.266	6.373
k_3	H, C−C or C−C, H	.4169	.4000
k_4	C≡C (C_2H_2)	15.568	15.342
	C≡C (others)	14.92	14.57
k_5	≡C−H	5.870	5.743

On the whole the agreement between the calculated and the observed frequencies is fairly good. The greatest discrepancy is for the C−C frequency of diacetylene. One general trend is observed. The calculated values for the C≡C frequencies are too high for methyl- and dimethylacetylenes. It appears that the carbon−carbon triple bond is weakened by the substitution of methyl groups for hydrogens.

In Table IV there are given the values of the force constants for liquids and for gases. Two sets of values are given for k_4, the first of which was used in the calculations. The second set was arrived at by approximate computations, and it should apply better for the substituted acetylenes. Except for the carbon−carbon single bond force constant, all of the force constants are larger for gases than for liquids. We have not yet arrived at any plausible explanation for the difference in behavior of the carbon−carbon single bond.

[6] Adel and Barker, J. Chem. Phys. **2**, 627 (1934); Badger, J. Chem. Phys. **5**, 178 (1937).

Interaction in Molecules Between Rotation and Slightly Anisotropic Oscillations

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The problem of the interaction between rotation and oscillation in two dimensionally slightly anisotropic molecules is considered quantum mechanically on the basis of model rotating only about an axis normal to the plane in which the oscillations take place. The energy of the molecule in the ground state becomes $(h/2)(\nu_1+\nu_2)+K^2h^2/8\pi^2A$ while for the upper states the energies are $E=h(\nu_1+\nu_2)+(K^2+\zeta^2)h^2/8\pi^2A\pm((\Delta\nu/2)^2+(Kh/4\pi^2A)^2\zeta^2)^{\frac{1}{2}}$, where ζ is a quantity depending upon the normal coordinates which in general is not an integer. The selection rules are such as to enhance the intensities of the set of lines in the sides of the two bands adjacent to each other at the expense of the set of lines in the sides of the bands farthest away from each other. The spacings between rotational lines of the first set converge rapidly toward a limiting value of $(1-\zeta)h/4\pi^2A$, while for the other set the spacings approach a value $(1+\zeta)h/4\pi^2A$.

I. INTRODUCTION

IT has been pointed out by several writers[1] that in polyatomic molecules where the symmetries are such that oscillations, isotropic in two or three dimensions (and therefore two or threefold degenerate), may take place, the interactions between rotation and oscillation will in general give rise to anomalous spacings between the rotation lines in an absorption band. This effect is directly associated with the fact that to an isotropic oscillation may always be ascribed a certain amount of angular momentum so that the total angular momentum of the molecule must be thought of as a kind of a vector sum of the angular momentum of the molecule rotating and the angular momentum of the molecule oscillating rather than, as is usually the case, consisting just of the angular momentum of rotation. If these vectors add up in one sense the rotational spacing will be larger than the normal spacing while if these angular momentum vectors add up in the opposite sense the spacing will be smaller than the normal spacing. These vectors may be said to add up in the positive sense or the negative sense depending upon whether or not the rotating electric moment is in the same sense or the opposite sense as the oscillational angular momentum vector. This might classically be equivalent to saying that in the first case the electric moment will rotate with a frequency in excess of the rotational frequency of the molecule while in the second case the opposite will occur.

When the isotropy is three demensional as is the case in the methane molecule, the spacings in nearly all the bands will be affected, while if the isotropy is confined to two dimensions, as is the case in the methyl halide molecules, so that the degenerate oscillations lie in a plane normal to the axis of symmetry, only the perpendicular bands, or those arising from oscillations lying in that plane, will be affected. For molecules like the methyl halides the two identical moments of inertia are much larger than the third, so that as is well known, the perpendicular bands will consist of a series of intense and nearly equally spaced lines protruding above a background made up of lines too closely spaced to be resolved spectroscopically. These rather intense lines protruding above the general background are known to arise when the molecule executes a rotational transition where $\Delta J=0$, $\Delta K=\pm1$, J and K being respectively the quantum number of total angular momentum and the quantum number of angular momentum about the axis of symmetry. Now these transitions are in reality just those which a rotator rotating in two dimensions only is permitted to make and for this reason it has been possible on the basis of a model where rotation occurs only about an axis normal to the plane in which the isotropic oscillations are contained to compute and predict

[1] E. Teller and Tiza, Zeits. f. Physik **73**, 791 (1932); E. Teller, *Hand und Jahrbuch der Chemie Physik*, Vol. 9 (1934), p. 125; D. M. Dennison and M. Johnston, Phys. Rev. **48**, 868 (1935).

quite accurately what the effect upon the appearance of the absorption band will be due to the interactions of the above kind.

In polyatomic molecules of even less degree of symmetry the two dimensional isotropy will in general disappear so that the oscillational degeneracies will be removed. One might quite well expect therefore, that such interactions as those described above would vanish. An interesting case arises, however, when one considers the case where the anisotropies are small so that the now nondegenerate vibration frequencies are separated by an interval $\Delta\nu$ which is of the same order of magnitude as the rotational frequencies that may occur in the band.[2] We shall here consider a case where two dimensionally slightly anisotropic oscillations occur and investigate what will be the nature of the interaction between these and the rotation of the molecule, examining at the same time what may be expected to be the effect on the observed spectrum. A complication is here clearly met with, namely, that in general, such molecules may no longer be categorized as symmetric, but rather as asymmetric rotators. If, however, we confine ourselves to such molecules which are only slightly asymmetric the rotational motion may still, to a good approximation, be represented by that of a symmetric top and then we may again base our predictions upon a model where rotation occurs only about an axis normal to the plane containing the two dimensionally slightly anisotropic oscillations.

II. Eigenvalues for a Rotating Anisotropic Molecule

The model which we shall consider is one in reality only of academic interest, but one which may be useful in interpreting certain of the bands in a coplanar XYZ_2 type of molecule of which the formaldehyde molecule is a well-known example. The X atom and the two Z atoms of such a molecule form an isoceles triangle with the Y atom located somewhere along the bisector of the vertex angle. In such a molecule, frequencies will occur which arise from oscillations of the electric moment at right angles to each other in a plane normal to the axis of symmetry of the molecule. Two such oscillations which may frequently be expected to lie not far removed from each other are the ones which may respectively be thought of as arising from a bending at the vertex of the YZ_2 triangle, which in first approximation is to be regarded as remaining rigid, of the XY arm of the molecule in the plane of the molecule and normal to it. The nature of these is perhaps better visualized by referring to Fig. 1 where it may be seen that

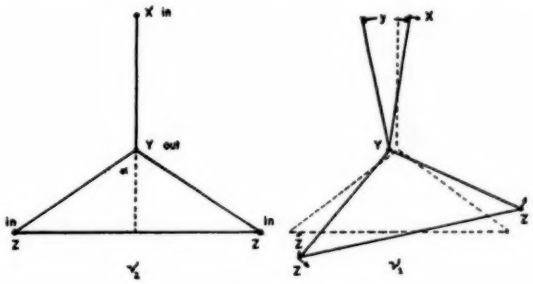

Fig. 1.

they correspond to actual deformations of the molecule. They are consequently often referred to as "deformation" frequencies. When such frequencies differ by only small amounts they will, as we shall see, when they are coupled to the rotation of the molecule, give rise to interesting interaction terms in the energy of the molecule.

The kinetic energy of the above molecule described in terms of a set of coordinates $x'y'$ and z' fixed in space will be:

$$T=\sum_{k=1}^{4}(m_k/2)(\dot{x}_k'^2+\dot{y}_k'^2+\dot{z}_k'^2), \qquad (1)$$

where m_1, m_2 and m_3 are the masses of the particles Z, X and Y, respectively. As we have indicated earlier, we shall consider the rotation of the molecule restricted so as to be only about an axis normal to the plane containing the two anisotropic oscillations. For this purpose a set of coordinates x, y and z rotating with the molecule is more suitable. We shall consider the z axis to be the axis of symmetry of the molecule about which the rotation is to take place and for convenience it is made to coincide with the space fixed z' axis. The following simple formulations relate the two sets of coordinates to each other: $x'=x\cos\varphi-y\sin\varphi$; $y'=x\sin\varphi+y\cos\varphi$; $z'=z$. In terms of these new coordinates the rest positions of the Z, X and Y particles shall

[2] E. B. Wilson, Jr., J. Chem. Phys. 4, 313 (1936).

be designated in the following manner: $x_1^0=-a$, $y_1^0=0$, $z_1^0=z_1^0$; $x_2^0=a$, $y_2^0=0$, $z_2^0=z_1^0$; $x_3^0=0$, $y_3^0=0$, $z_3^0=z_3^0$; $x_4^0=0$, $y_4^0=0$, $z_4^0=z_4^0$. Since the YZ_2 triangle is to be regarded as rigid we have that $x_1=x_2$ and $y_1=y_2$, x_1, x_2, y_1 and y_2 being the displacements along the x and y axes of the Z particles. By fixing the center of gravity of the molecule at the origin of the coordinate system and setting the linear and angular momenta equal to zero we have further that $x_3=cx_1$, $x_4=dx_1$, $y_3=c'y_1$, $y_4=d'y_1$, x_3, x_4, y_3 and y_4 being the displacements along the x and y axes of the X and Y particles. The constants c, d, c' and d' are abbreviations for the following quantities:

$$c=-(2m_1(2m_1+m_4)z_1^0+2m_1m_3z_3^0)/(m_3(m_3+m_4)z_3^0+2m_1m_3z_1^0),$$
$$d=-2m_1(z_3^0-z_1^0)/((m_3+m_4)z_3^0+2m_1z_1^0);$$
$$c'=-(2m_1(2m_1+m_4)z_1^0+2m_1m_3z_3^0+2m_1m_4y_1^0)/(m_3(m_3+m_4)z_3^0+2m_1m_3z_1^0) \text{ and}$$
$$d'=-2m_1(z_3^0-z_1^0-y_1^0)/((m_3+m_4)z_3^0+2m_1z_1^0).$$

Finally we have also that $z_1=-z_2$ where these are the components along the z axis of the actual displacements of the Z particles in the yz plane from their positions of rest. It is convenient also to make the further substitutions:

$$x=\tfrac{1}{2}((1-d)z_3^0-(c-1)z_4^0-(2-c-d)z_1^0)x_1/(z_3^0-z_4^0) \text{ and}$$
$$y=((1-d')z_3^0-(1+c'-2d')z_4^0-(c'-d')z_1^0)y_1/(z_4^0-z_1^0).$$

The variables z_1 and z_2 are, however, not independent variables, but as may be seen from Fig. 1, are related to y_1 and y_4 in the following manner: $z_1=-z_2=(y_4-y_1)\tan\alpha$ where α is equal to half the $Z-Y-Z$ angle. Replacing $\dot{z}_1$ by its equivalent $(d'-1)\dot{y}_1\tan\alpha$, the relation (1) becomes transformed into:

$$T=(\mu/2)(\dot{x}^2+x^2\dot{\varphi}^2)+(\mu'/2)(\dot{y}^2+y^2\dot{\varphi}^2)+\mu''(x\dot{y}-\dot{x}y)\dot{\varphi}+(A/2)\dot{\varphi}^2 \quad (2)$$

μ in the above being an abbreviation for: $4(2m_1+m_3c^2+m_4d^2)(z_3^0-z_4^0)^2/((1-d)z_3^0-(c-1)z_4^0-(2-c-d)z_1^0)^2$, μ' for $(2m_1+2m_1(d'-1)^2\tan^2\alpha+m_3c'^2+m_4d'^2)(z_4^0-z_1^0)^2/((1-d')z_3^0-(1+c'+2d')z_4^0+(c'-d')z_1^0)^2$, μ'' for $2(2m_1+m_3cc'+m_4dd')(z_4^0-z_1^0)(z_3^0-z_4^0)/((1-d)z_3^0-(2-c-d)z_1^0-(c-1)z_4^0)((1-d')z_3^0-(1+c'+2d')z_4^0-(c'-d')z_1^0)$ and A for the moment of inertia $2m_1a^2$ of the molecule.

The potential energy of the molecule expressed in these coordinates may be taken to be:

$$V=(2\pi^2\mu\nu_1^2)x^2+(2\pi^2\mu'\nu_2^2)y^2 \quad (3)$$

so that the quantum-mechanical equation appropriate for our problem may, neglecting certain terms which will be small, be found to be:

$$\{(\mu'/\mu)\partial^2/\partial x^2+\partial^2/\partial y^2+(\mu'/A)((u'/\mu)y^2\partial^2/\partial x^2-(\mu/\mu')x^2\partial^2/\partial y^2-(\mu''^2/\mu\mu')(y\partial/\partial y+2xy\partial/\partial y\partial/\partial x+x\partial/\partial y))+(\mu'/A)\partial^2/\partial\varphi^2-2(\mu'/A)(\mu''/\mu')(y\partial/\partial x-x\partial/\partial y)\partial/\partial\varphi+(8\pi^2\mu'/h^2)(E-(2\pi^2\mu\nu_1^2)x^2-(2\pi^2\mu'\nu_2^2)y^2)\}\Psi=0. \quad (4)$$

It is convenient to introduce the notation $\alpha=(4\pi^2\mu\nu_1/h)$ and $\beta=(4\pi^2\mu'\nu_2/h)$ in the above as well as to affect the changes of variable $\xi=\alpha^{\frac{1}{2}}x$ and $\eta=\beta^{\frac{1}{2}}y$. Noting further that φ is ignorable so that Ψ may be written $F(\xi,\eta)\exp(iK\varphi)$, K being as usual integral Eq. (4) becomes transformed into:

$$\{(\alpha\mu'/\mu)\partial^2/\partial\xi^2+\beta\partial^2/\partial\eta^2+(\mu'/A)((\alpha\mu'/\beta\mu)\eta^2\partial^2/\partial\xi^2+(\beta\mu/\alpha\mu')\xi^2\partial^2/\partial\eta^2-(\mu''^2/\mu\mu')(\eta\partial/\partial\eta+2\eta\xi\partial/\partial\xi\partial/\partial\eta+\xi\partial/\partial\xi))-(2iK\mu'/A)(\mu''/\mu')((\alpha/\beta)^{\frac{1}{2}}\eta\partial/\partial\xi-(\beta/\alpha)^{\frac{1}{2}}\xi\partial/\partial\eta)+(\lambda-(\alpha\mu'/\mu)\xi^2-\beta\eta^2)\}F(\xi,\eta)=0 \quad (5)$$

λ being made to replace $(8\pi^2\mu'E/h^2)-\mu'K^2/A$.

Equation (5) lends itself readily to solution only when $\alpha=(\alpha\mu'/\mu)=\beta$ in which case the problem degenerates to that of a two-dimensional isotropic oscillator rotating about an axis normal to its own plane. If, however, we confine ourselves to such molecules where the anisotropy is small so that $\langle\alpha,\rangle(\alpha\mu'/\mu)$ and β are not greatly unlike, the equation is still exactly soluble when one neglects certain terms of the order of magnitude $(\Delta\nu/\nu)(h/4\pi^2A)$ i.e., small as compared with the rotational frequencies of the molecule and which in first approximation need not be taken into account. We shall confine ourselves to the fundamental bands only so that it will be sufficient to obtain the solution and eigenvalues to Eq. (5) for the lowest and the first excited states only. Neglecting the above terms, we may take $F(\xi,\eta)$ for the ground state to be $F(\xi,\eta)=(\alpha\beta/\pi^2)^{\frac{1}{4}}\exp-(\xi^2+\eta^2)/2$ which yields as the energy value the following:

$$E(0,K)=(h/2)(\nu_1+\nu_2)+K^2h^2/8\pi^2A, \quad (6)$$

h being as usual Planck's constant, ν_1 and ν_2 the frequencies of the two oscillations and A the moment of inertia. For the two excited states there will be two functions $F(\xi,\eta)$ which will equally well satisfy Eq. (5), namely $\varphi_1=2\eta \exp -(\xi^2+\eta^2)/2$ and $\psi_1=2\xi \exp -(\xi^2+\eta^2)/2$. Substituting these into (5) one obtains respectively as the first-order terms the following:

$$\{(\lambda-\beta-3(\alpha\mu'/\mu)-(\mu''^2/\mu\mu')(\mu'/A)) -(2iK\mu'/A)(\mu''/\mu')(\eta/\xi)(\nu_1/\nu_2)^{\frac{1}{2}}\}\psi_1=0,$$

$$\{(\lambda-3\beta-(\alpha\mu'/\mu)-(\mu''^2/\mu\mu')(\mu'/A)) +(2iK\mu'/A)(\mu''/\mu')(\xi/\eta)(\nu_2/\nu_1)^{\frac{1}{2}}\}\varphi_1=0,$$

which, observing that the operators ξ/η and η/ξ operating on φ_1 and ψ_1 respectively convert them into ψ_1 and φ_1, yield at once the linear homogeneous equation:

$$[(\lambda-\beta-3(\alpha\mu'/\mu)-(\mu''^2/\mu\mu')(\mu'/A))]\psi_1 -(2iK\mu'/A)(\mu''/\mu')(\nu_1/\nu_2)^{\frac{1}{2}}\varphi_1=0, \quad (7)$$

$$(2iK\mu'/A)(\mu''/\mu')(\nu_2/\nu_1)^{\frac{1}{2}}\psi_1+[(\lambda-3\beta -(\alpha\mu'/\mu)-(\mu''^2/\mu\mu')(\mu'/A))]\varphi_1=0.$$

The determinant of the coefficients of φ_1 and ψ_1, vanishing, will serve to determine the eigenvalues of the molecule for the first excited states. Diagonalizing the energy matrix, one obtains:

$$E(1,K)=h(\nu_1+\nu_2)\pm h((\nu_1-\nu_2)^2/4 +(K\zeta h/4\pi^2A)^2)^{\frac{1}{2}}+(K^2+\zeta'^2)(h^2/8\pi^2A). \quad (8)$$

where

$$\zeta=(\mu''/\mu') \quad \text{and} \quad \zeta'^2=(\mu''^2/\mu\mu').$$

The characteristic functions for these states will be linear combinations of φ_1 and ψ_1, the coefficients in each case being given by the minors of the determinant (7) upon substitution for λ the root corresponding to that state. Designating by $\Psi(+1)$ and $\Psi(-1)$ the characteristic functions whose eigenvalues are respectively obtained by using the *plus* and the *minus* signs before the radical in Eq. (8), we obtain after normalization:

$$\begin{aligned}\Psi(+1)&=N\{(iK\zeta h^2/4\pi^2A)(\nu_2/\nu_1)^{\frac{1}{2}}2\eta \\ &\quad +h[(\nu_1-\nu_2)/2+((\nu_1-\nu_2)^2/4 \\ &\quad +(K\zeta h/4\pi^2A)^2)^{\frac{1}{2}}]2\xi\}e^{-(\xi^2+\eta^2)}/2, \\ \Psi(-1)&=N\{-ih[(\nu_1-\nu_2)/2+((\nu_1-\nu_2)^2/4 \\ &\quad +(K\zeta h/4\pi^2A)^2)^{\frac{1}{2}}]2\eta \\ &\quad +(K\zeta h/4\pi^2A)(\nu_1/\nu_2)^{\frac{1}{2}}2\xi\}e^{-(\xi^2+\eta^2)}/2, \\ N^2&=\{h^2[(\nu_1-\nu_2)/2+((\nu_1-\nu_2)^2/4 \\ &\quad +(K\zeta h/4\pi^2A)^2)^{\frac{1}{2}}]^2 \\ &\quad +(K\zeta h/4\pi^2A)^2(\nu_k/\nu_j)\}^{-1}(4\pi^2\mu\nu_1\nu_2/h^2)^{\frac{1}{2}},\end{aligned} \quad (9)$$

k and j being respectively 1 and 2, and 2 and 1 when N is used with the first and the second functions.

Before approaching the question of what will be the selection rules for such a molecule as the above and what effect these interactions might be expected to produce on the intensities of the lines in a band it will be convenient to note how the energies and the eigenfunctions will behave in two limiting cases. In the one limiting case where $\nu_1-\nu_2$ approaches zero so that it may be considered negligible with respect to $Kh/4\pi^2A$, Eqs. (6) and (8) degenerate into $h\nu+K^2h^2/8\pi^2A$ and $2h\nu+(K\pm\zeta)^2h^2/8\pi^2A$, respectively, which are just the energies of a two-dimensionally isotropic oscillator rotating in its own plane as determined by Teller and Tiza. Letting $\eta=\rho \sin\theta$ and $\xi=\rho\cos\theta$ the characteristic functions degenerate into $(\alpha/\pi)^{\frac{1}{2}} \exp(-\rho^2/2)$ for the ground state and into $(\alpha/2^{\frac{1}{2}}\pi)^{\frac{1}{2}}\rho \exp(-\rho^2/2)\exp(i\theta)$ and $(\alpha/2^{\frac{1}{2}}\pi)^{\frac{1}{2}}\rho\exp(-\rho^2/2)\exp(-i\theta)$, complex conjugates of each other, for the upper state.

The other limiting case arises when $\nu_1-\nu_2$ is so large with respect to $K\zeta h/4\pi^2A$ that the latter may entirely be neglected. The energy values (6) and (8) then reduce to $(h/2)(\nu_1+\nu_2)+K^2h^2/8\pi^2A$ for the ground state and for the upper state $(h/2)(3\nu_1+\nu_2)+K^2h^2/8\pi^2A+$const. and $(h/2)(\nu_1+3\nu_2)+K^2h^2/8\pi^2A+$const. These are just the energy values which one would obtain when one assumes that the quantum mechanical equation is exactly separable in the coordinates of rotation and oscillation. The two states will now have become completely separated and the functions characterizing them will according to (9) take just the anticipated values:

$$\Psi(+1)=(\alpha\beta/2\pi^2)^{\frac{1}{2}}(2\xi\exp-(\xi^2+\eta^2)/2)$$
$$\text{and } \Psi(-1)=(\alpha\beta/2\pi^2)^{\frac{1}{2}}(2\eta\exp-(\xi^2+\eta^2)/2).$$

We might therefore expect such a molecule as the above, for small values of the rotational quantum number K where $\Delta\nu$ could be considered large compared to $K\zeta h/4\pi^2A$ to behave very much like a molecule of the latter limiting case, but as K increases so that $K\zeta h/4\pi^2A$ becomes of the same magnitude and eventually large as compared with $\Delta\nu$, that it would approximate more nearly the first limiting case in its behavior.

III. Selection Rules and the Question of Intensities

The final conclusions of the previous section may be confirmed quantitatively by a study of the selection rules and the intensity relations. The rules of transition may be arrived at by examination of the nonvanishing matrix components of the electric moment as the molecule executes a transition from the ground state to one of the two characterized either by $\Psi(+1)$ or $\Psi(-1)$. Since the method is an obvious one, we shall not here derive them, but content ourselves merely by stating what they are. When a transition from the zeroth vibration state to one of the two upper states takes place the selection rule for K will in general be $\Delta K=\pm 1$, lines in the spectrum occurring at the following corresponding frequency positions:

$$\nu=(\nu_1+\nu_2)/2\mp(Kh/4\pi^2A) \pm\{(\nu_1-\nu_2)^2/4+(K\zeta h/4\pi^2A)^2\}^{\frac{1}{2}}. \quad (10)$$

From this it will be seen that when $\Delta\nu$ is large compared with $K\zeta h/4\pi^2A$ the spacing between rotational lines approaches the normal value $h/4\pi^2A$, but as K increases, taking like signs in (10), the spacing approaches $(1+\zeta)h/4\pi^2A$; taking opposite signs in (10), a value approaching $(1-\zeta)h/4\pi^2A$ prevails. Examination of the matrix components verifies, moreover, that when the molecule executes an oscillational transition from the ground state to the state $+1$, the probability of the rotational transition $K=K'+1$ in the lower to $K=K'$ in the upper state increases at the expense of the transition $K=K'-1$ to $K=K'$, as K increases. Similarly, when the molecule makes a transition from the ground state to the oscillational state -1, the transition $K=K'-1$ to $K=K'$ increases in probability at the expense of the other.

This result is again consistent with the work of Teller and Tiza in which they showed that for a two dimensional isotropic oscillator rotating in its own plane, ζ being taken as unity, the rotational structure would collapse into a single line, i.e., the spacing between two adjacent lines would be zero. This is virtually what happens in our case as $Kh/4\pi^2A$ becomes large compared to $\Delta\nu$.

In conclusion we shall simply summarize the derived results. In certain molecules when oscillations occur which are only slightly anisotropic interactions between rotation and oscillation may occur, not wholly unlike those that take place in completely symmetric molecules. The effect upon the spectrum will be a rapid convergence of the rotational lines in the halves of the two bands adjacent to each other toward a limiting value of the spacings $(1-\zeta)h/4\pi^2A$, while on the other sides the spacings between lines rapidly approach a value $(1+\zeta)h/4\pi^2A$. The intensities of the former set of lines will at the same time be enhanced at the expense of the latter set of lines.

The author desires to express his gratefulness to Professor E. Teller and to Professor D. M. Dennison with whom he has had occasion to discuss this problem and who have made suggestions distinctly helpful in deducing the results in the present formulation.

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Two Bands in the Infrared Spectrum of Formaldehyde

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Two infrared bands of the type arising from oscillations of the electric moment normal to the axis of symmetry have been measured under high dispersion and identified as the two oscillations which are at right angles to each other and which in Sutherland and Dennison's notation are ν_5 and ν_6. Their centers are respectively at 1278 cm^{-1} and 1165 cm^{-1}. The anomalous spacing between the principal rotation lines is accounted for on the basis of an interaction between rotation and the two oscillations which are only slightly anisotropic.

I. Introduction

IT has been possible by measurements on the absorption by formaldehyde vapor in the ultraviolet[2] and infrared regions[3] of the spectrum to accurately determine the magnitudes of the moments of inertia of this molecule. Concerning what are to be taken to be the fundamental vibration frequencies, however, considerable ambiguity has existed, for while the five bands in the region 3.0μ to 7.0μ may definitely be identified, no such identification for the remaining bands from 7.0μ on has until now seemed possible. Neither has it been possible to enlist any aid in this matter from the Raman spectrum which has only been investigated for formaldehyde in solutions. Four investigators[4] of the Raman spectrum of formaldehyde in solution following different methods of procedure, draw the unanimous conclusion that the standard 40 percent water solution cannot give rise to the fundamental frequencies characteristic of H_2CO, but that the lines observed must be attributed to products of hydration or of polymerization—a conclusion supported also by other physical evidence.[5] Certain authors have drawn upon the results of a fifth investigator[6] of the Raman spectrum of formaldehyde in solution for the purpose of assigning vibration frequencies to the H_2CO molecule, apparently without too close scrutiny of its validity for the purpose. The measurements are reported to be on an 80 percent solution but which we are inclined to interpret as a misprint intended to read 30 percent. Our belief is based upon the experience of one of us in an attempt to make Raman measurements on pure liquid formaldehyde and on concentrated solutions as well (all of which were maintained at $-78.5°C$ and illuminated by radiation of wave-length 4358A only) which failed because of the too rapid polymerization of the formaldehyde at the walls of the Raman tube. Even if the solution in the above were of a concentration of 80 percent we do not feel that these frequencies may unequivocally be assigned to the formaldehyde molecule for of the six lines reported, all except the one at 1768 cm^{-1} fall at positions coincident with lines, reported also by the other four investigators, concerning which there is general agreement. It seems only natural to ascribe these lines also to products of hydration or polymerization since it is difficult to believe that such products would not also be present in a solution of formaldehyde in 80 percent concentration.

To help clarify what are the actual facts concerning the fundamental bands due to the formaldehyde molecule we have remeasured the entire spectrum of the vapor from 1.0μ to 15.0μ using a prism spectrometer of the Wadsworth-Litrow type. In addition the entire spectral range 7.0μ to 12.0μ has been investigated under high dispersion using a prism-grating spectrometer.

II. Experimental

An important advance in the experimental technique over that of other attempts is the improved absorption cell here used in making these measurements. This cell was actually developed in preparation for the measurements which we proposed to make on the isotopic formaldehydes.[7] The small amounts of these compounds which were available prevented employing the older method of displacing the air in the cell by formaldehyde vapor and necessitated constructing a cell which would remain vacuum tight up to 200°C. This was accomplished, however, by sealing the joints which the polished rocksalt windows make with the ground ends of the glass tube of which the cell was made with glyptal (No. 1201). These cells were eminently satisfactory and have been operated at temperatures as high as 250°C without any signs of deterioration. No difficulty was experienced from the unequal expansion of the glass and the rocksalt during the raising of these cells to their desired temperatures since the glyptal takes an appreciable time to lose its elasticity. On cooling, however, strains were produced which frequently cracked the halite windows or broke it loose from the glass tube.

[1] Fellow of the Royal Society of Canada.
[2] G. H. Diecke and G. B. Kistiakowsky, Phys. Rev. **45**, 4 (1934).
[3] Harald H. Nielsen, Phys. Rev. **46**, 117 (1934).
[4] Kohlrausch and F. Köppl, Zeits. f. physik. Chemie **24**, 370 (1934); P. Krishnamurti, Ind. J. Phys. **6**, 309 (1931); James H. Hibben, J. Am. Chem. Soc. **53**, 2418–9 (1931); B. Trumpy, Klg. Norske Videnskab Selskabs Skrifter **9**, 1–20 (1935).
[5] Frederic Walker, J. Phys. Chem. **35**, 1104 (1931); V. Henri and A. Schou, Zeits. f. Physik **49**, 774 (1928).
[6] N. Pal and Sen Gupta, Ind. J. Phys. **5**, 24 (1930).
[7] To be published soon.

The cells of the above type were 7 cm long and 5 cm in diameter. They were evacuated and tested before a weighed sample of paraformaldehyde sufficient to yield enough formaldehyde vapor to produce the desired absorption (generally enough to produce formaldehyde vapor to a pressure of about 20 cm Hg) was introduced. The cell was then evacuated, sealed off and raised to a temperature above that required for complete sublimation.[8] Besides economizing on the material a cell such as that described above possesses the other obvious advantage of insuring that no oxidation of the formaldehydes could take place. This cell was used for all the measurements made with the prism spectrometer and for many of the high dispersion measurements as well.

It is clearly desirable, if possible, to make the high dispersion measurements at room temperature. It was found possible to do this in the following manner. To a cell similar to the one described above, 27 cm long was joined a trap which in turn was joined to a reservoir containing polymerized formaldehyde which had been purified according to the method of Spence and Wild.[9] The entire system was evacuated and sealed off and then the formaldehyde was sublimed over into the trap where it was collected as a liquid by a freezing bath kept at a temperature of −78.5°C. At this temperature the liquid formaldehyde, which is monomeric, has a vapor pressure of 22 mm[9] Hg. The 27 cm cell filled with formaldehyde vapor at this pressure offers a path length of sufficient magnitude for the absorption measurements to be readily made. Polymerization of the vapor on the walls and windows of the cell occurs slowly at this pressure and the cell may be used with confidence for about four hours. The cells were then taken apart and completely rebuilt. The measurements obtained using this cell were found to duplicate those obtained when the heated cell was used except that in the former case the lines were noticeably sharper and more details in the absorption pattern were discernible. For the exploratory prism work, a prism spectrometer of the Wadsworth-Litrow type was available. It was used only to verify the results obtained in the earlier investigation and to extend the exploration from 11.0μ to 15.0μ. The spectrometer used to make the high dispersion measurement was the same used in other experiments carried out in this laboratory and is capable of resolving lines separated by frequency intervals of less than 1 cm^{-1}. Two gratings were used in making the measurements from 7.0μ to 12.0μ, one ruled by R. W. Wood with 800 lines per inch and another with 1200 lines per inch. The latter was most generously loaned to us by Professor H. M. Randall for these measurements.

[8] A rough determination of the vapor pressure of paraformaldehyde yielded the following results:

T°C	30	65	80	90	100	110	120
P mm Hg	0	156	246	331	372	401	586

[9] R. Spence and W. Wild, J. C. S. 507 (1935); R. Spence and W. Wild, J. C. S. 338–40 (1935).

III. Experimental Results

The absorption spectrum of formaldehyde as determined prismatically is shown in Fig. 1 and confirms in general appearance the prism curve of Nielsen although the present one seems to indicate more continuous absorption from 7.5μ on. This may be due in part to the somewhat better resolving power of the prism instrument used in the earlier experiment. Regions of intense absorption occur near 3.5μ, 5.7μ, 6.7μ and 7.5μ to nearly 10μ, but beyond these no evidence of any absorption bands could be found.

The region from 7.5μ to 10μ was found to consist of two rather intense and overlapping bands, having the characteristics of oscillations

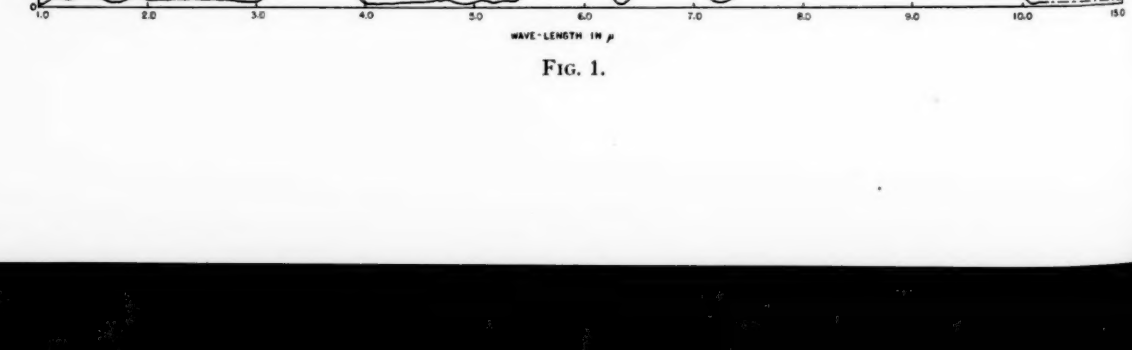

Fig. 1.

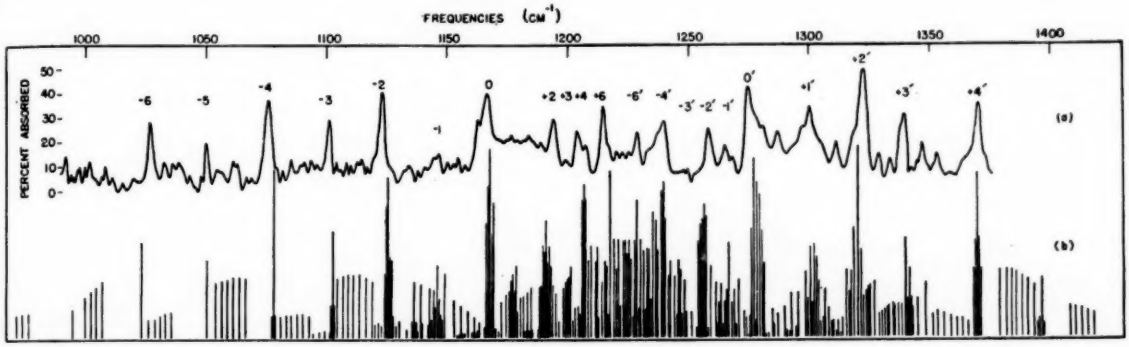

FIG. 2.

perpendicular to the axis of symmetry. From 7.5μ to beyond 8.0μ the region duplicates almost exactly the data reported by Nielsen, except that with the cell operated at room temperatures considerably more detail was to be found. As reported in our preliminary communication,[10] the data from this point on was entirely different from those of Nielsen. The band reported by him was of the type arising from an oscillation parallel to the axis of symmetry of the molecule while that which here is found is another band of the type where the electric moment oscillates perpendicular to this axis. It is probably to be concluded that the earlier reported band was due to some impurity present, perhaps some product of oxidation, but certainly not to formaldehyde. It is to be noted also that the spacings between the lines of this band reported in the earlier work are slightly less than those in other bands of this type. In all events the measurements on this region have been repeated a great many times and under varied conditions, but the pattern has consistently repeated itself. In Fig. 2 (a) is reproduced the absorption pattern of this region as it was observed with the cell operated at room temperature. Our Fig. 2 (a) embraces the region 9.6μ reported by Nielsen to and including the lines given by him in his Fig. 5. One additional line has been added to this latter group. In Table I are given the frequency positions of the principal lines in the band. The convergence of these so noticeable in Nielsen's Fig. 5 is here shown by the additional detail we have observed to be only an apparent one. The fact that the spacings between the rotational lines in the extremities of the two bands is something over 23 cm^{-1} or nearly 50 percent larger than those in the similar type of band near 3.5μ in the spectrum of formaldehyde is a detail worthy of some note.

IV. Discussion of the Results

These rather intense bands comprising the region from 7.5μ to 10μ and here measured under high dispersion must undoubtedly be taken to be the so-called "deformation" frequencies which in Sutherland's and Dennison's[11] notation are ν_5 and ν_6. As to which is which of the two frequencies is more difficult to ascertain, however. Our most likely avenue of successfully identifying these is by a study of the rotational structure. The formaldehyde molecule, considered as a rotating body, is a slightly asymmetric top so that these two oscillations which are both normal to the axis of symmetry (i.e., the one is perpendicular to the plane of the molecule while the other remains in the plane) might be expected to produce bands whose rotational structure would in a general way be similar except near the centers. These lines near the center which are the only ones really affected by the asymmetry become split up into components here too closely spaced for spectroscopic resolution and would appear rather as broadened lines. The manner in which this broadening takes place, however, is different for the two lines nearest the center in each of the two bands. For the oscillation out of the plane the two central lines converge toward each other giving an apparent spacing between these something less

[10] E. S. Ebers and H. H. Nielsen, J. Chem. Phys. **5**, 84 (1937).

[11] G. B. B. M. Sutherland and D. M. Dennison, Proc. Roy. Soc. **148A**, 250 (1935).

than that between any of the other lines in the band, while for the oscillation remaining in the plane, the central lines converge away from each other producing a spacing between them larger than that between other lines in the band.

The two bands lie, moreover, very close together; separated from each other by an interval $\Delta\nu$ of only slightly more than 100 cm^{-1}. The frequencies are therefore only slightly anistropic and interactions between rotation and oscillation may therefore be expected to occur of the type discussed by one of us.[12] We shall assume further that this type of interaction does not here materially alter the asymmetry of the molecule so that the energies of the molecule rotating and oscillating in these modes may to a good approximation be written:

$$E=\frac{h}{2}(\nu_5+\nu_6)+\left(\frac{h^2}{8\pi^2}\right)\frac{J(J+1)}{2}\left(\frac{1}{A_x}+\frac{1}{A_y}\right)-\frac{Wh^2}{8\pi^2}\left[\frac{1}{2}\left(\frac{1}{A_x}+\frac{1}{A_y}\right)-\frac{1}{A_z}\right] \quad (1)$$

for the ground state and:

$$E=h(\nu_5+\nu_6)+\frac{h^2}{8\pi^2}(J(J+1)-W)(1/2A_x+1/2A_y)+\frac{(W+\zeta^2)h^2}{8\pi^2A_z}\pm h\left[\left(\frac{\nu_5-\nu_6}{2}\right)^2+W\left(\frac{h\zeta}{4\pi^2A_z}\right)^2\right]^{\frac{1}{2}} \quad (2)$$

for the first excited states where W are the roots of the Wang-Klein[13] secular determinant for the eigenvalues of the asymmetric rotator and which may perhaps most readily be obtained from the equations of Nielsen.[14] In our case these will approximately be equal to K^2, K taking all integral values from zero to J, the quantum number of total angular momentum. An approximate value for the constant ζ occurring in the above equation has been calculated in reference 12 on the basis of a model where the CH_2 triangle remains rigid and may be seen to have an involved dependence on the normal modes of the oscillations. Replacing W by K^2 in (1) and (2) and observing that in the case of a symmetric top that the strong lines in a perpendicular band like the ones here observed which protrude above the background are obtained when the molecule executes a transition of the type $\Delta J=0$, $\Delta K=\pm1$, one obtains the following approximate relation for the frequency positions of the lines in the two bands:

$$\nu=(\nu_5+\nu_6)/2+(h/8\pi^2)(\tfrac{1}{2}(1/A_x+1/A_y)+(\zeta^2-1)/A_z)+(Kh/4\pi^2)(\tfrac{1}{2}(1/A_x+1/A_y)-1/A_z)\pm((\nu_5-\nu_6)^2/4+(Kh/4\pi^2A_z)^2), \quad (3)$$

K taking the values 0, ±1, ±2, etc. the effect of this interaction on the spectrum will be seen from (3) to be, to give spacings between the principal rotational lines in the extremities of the bands farthest away from each other and in the sides nearest each other, the values $(h/4\pi^2)\times(\frac{1}{2}(1/A_x+1/A_y)-(1\pm\zeta)/A_z)$, respectively. It will be seen that the spacings actually observed between these principal lines ultimately reached here would perhaps be about 26 cm^{-1}. Actual quantitative agreement between predicted lines and experimentally observed lines is approached when one takes

$$\nu_5+(h/8\pi^2)(\tfrac{1}{2}(1/A_x+1/A_y)+(\zeta^2-1)/A_z)$$

and,

$$\nu_6+(h/8\pi^2)(\tfrac{1}{2}(1/A_x+1/A_y)+(\zeta^2-1)/A_z),$$

respectively, equal to 1278 cm^{-1} and 1165 cm^{-1}, $(h/4\pi^2)(1/A_z-\frac{1}{2}(1/A_x+1/A_y))=16.2$ cm^{-1} and ζ equal to about 0.80. Applying the approximate value of ζ computed in reference 12 to the molecular model of formaldehyde proposed by

TABLE I. *Frequencies of principal absorption lines for the region 7.0μ–10μ.*

Line No.	Frequencies in cm^{-1}	Line No.	Frequencies in cm^{-1}
−6	1027.0	−6′	1229.1
−5	1051.0	−4′	1239.3
−4	1075.9	−3′	——
−3	1099.7	−2′	1259.0
−2	1121.8	−1′	1265.3
−1	1146.3	0′	1275.2
0	1165.7	+1′	1300.8
+1	——		1312.3
+2	1093.4	+2′	1323.0
+3	——	+3′	1339.4
+4	1204.6		1347.0
+6	1213.8	+4′	1370.5

[12] Harald H. Nielsen, J. Chem. Phys. **5**, 818 (1937).
[13] S. C. Wang, Phys. Rev. **34**, 243 (1929); O. Klein, Zeits. f. Physik **58**, 730 (1929).
[14] Harald H. Nielsen, Phys. Rev. **38**, 1432 (1931). In the equations for W given in this paper, several errors occur, some of which are misprints and others which apparently are due to errors in copying from the original manuscripts. Corrections to these may be found in a paper by Randall, Dennison, Ginsberg and Weber, Phys. Rev. **52**, 160 (1937).

Diecke and Kistiakowsky where the H−C−H bond angle is taken to be tetrahedral one obtains a value of ζ equal to about 0.6. Considering the approximations made in these calculations this value seems in satisfactory agreement with the experimentally determined value. In computing the energies (1) and (2) from which the predicted lines are calculated, actual W values, and not merely the approximate ones $W=K^2$ were used. The W values actually employed were the same determined by Nordsieck[15] in calculations made by him on the appearance of the infrared bands of formaldehyde.

The alternating intensities of the principal lines as observed in the two bands are readily accounted for when one considers the presence of the two identical hydrogen atoms each with a nuclear spin $\frac{1}{2}(h/2\pi)$. This serves to divide the molecular energy states into a symmetric and an antisymmetric classification in the following manner. The complete wave function Ψ for a state will be a product of the following functions; the electronic wave function Φ, the oscillational wave function $R(v_1, v_2, v_3, v_4, v_5, v_6)$, the rotational wave function $\Theta(J, \tau, M)$ and the nuclear spin function S. The number τ occurring in Θ is the parameter introduced by Dennison[16] and takes the $2J+1$ values $-J$ to J, the state of lowest energy for any value of J being that characterized by $\tau=-J$.

The symmetry character of Φ for an interchange of the two identical hydrogen nuclei is unknown to us; R, however, is a symmetric function when all the v's are zero, but antisymmetric when either v_5 or v_6 becomes one, all the others remaining zero. The symmetry character of the function Θ for a molecule like H_2CO where the axis of the least moment of inertia bisects the bond angle of the carbon has been discussed by Dennison and is independent of J. For any value of J, it is alternatingly symmetric, antisymmetric; antisymmetric, symmetric beginning always as symmetric for $\tau=-J$. Applying the general exclusion principle for protons which states that only such energy states are permitted to exist where the entire Ψ function is antisymmetric for an interchange of these, we see that the rotational levels will be divided into two groups, those having a symmetric and those having an antisymmetric nuclear spin function. Of these the first have a weight factor 3 as compared to a weight factor 1 for the second. Having determined

$$\nu_5+(h/8\pi^2)[\tfrac{1}{2}(1/A_x+1/A_y)+(\zeta^2-1)/A_z],$$
$$\nu_6+(h/8\pi^2)[\tfrac{1}{2}(1/A_x+1/A_y)+(\zeta^2-1)/A_z],$$

respectively, to be 1278 cm^{-1} and 1165 cm^{-1}, bearing in mind that the lines occurring at these points arise from transitions $J=J$, $\tau=-J+1 \rightarrow J=J$, $\tau=-J$ or $J=J$, $\tau=-J+2\rightarrow J=J$, $\tau=-J$ (i.e., $J=J$, $K=1\rightarrow J=J$, $K=0$ in the case of the symmetric top) and noting, moreover that these lines are *strong* lines, we have also determined that the levels $J=J$, $\tau=-J+1$, $\tau=-J+2$ have in the ground state a symmetric spin function. Thus the spin function (and as well the weight factor) to be associated with any level in the ground state has uniquely been determined. In the first excited states this classification will be just completely reversed because the function R is here antisymmetric. It may be seen, moreover, that the electronic part of the wave function must be symmetric for an interchange of the two identical hydrogen nuclei. From the above it becomes clear that the principal lines in the bands should be expected to occur alternately strong and weak on either side beginning with an intense line for the transition $J=J$, $\tau=-J+1$, $-J+2\rightarrow J=J$, $\tau=-J$.

The lines predicted by the permitted transitions between the energy levels computed from (1) and (2), using J values up to and including $J=10$, have for the sake of convenient comparison been plotted with their appropriate intensities in Fig. 2 (b) directly below the experimentally observed spectrum. While certainly additional lines will arise from levels of J value greater than 10, they will serve principally to fill out the background of the band which is here experimentally unresolved. The additional labor involved in computing the values of W has not seemed justifiable considering what might be gained in the actual agreement to be had between theory and experiment. In general we feel the agreement between the theoretically predicted spectrum and the experimentally observed spectrum as shown in Figs. 2 (a) and 2 (b) to be a satisfactory one when one considers the approximations that have been made.

[15] A. Nordsieck, Phys. Rev. **45**, 133–4 (1934).
[16] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

The Dielectric Constant of Isopropyl Alcohol Vapor

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The dielectric constant of isopropyl alcohol vapor has been measured at 12 different temperatures between 26.8°C and 190.4°C. At each temperature, measurements were made at many different vapor pressures. It is emphasized that this procedure is highly desirable. The slope, obtained by least squares, of the resulting $(K-1)/(K+2)$ *versus* pressure curve gives one point on the Debye line. Twelve such points were obtained. Unusually pure isopropyl alcohol was used. The data fall on a Debye line whose equation as obtained by least squares is: $[(K-1)/(K+2)]RT/p' = (17.40\pm0.41)+(17{,}490\pm155)/T$. This yields a value $(1.682\pm0.007)\times10^{-18}$ e.s.u. for the electric moment of the isopropyl alcohol molecule. These results agree closely with some previously unreported measurements made by the author three years ago.

IT is becoming more and more important to have available reliable values for the permanent electric moments of various molecules. A survey of the literature covering dielectric studies of dilute solutions shows that a large number of electric moments obtained therefrom appear inconsistent. Numerous of these inconsistencies may disappear when the effect of the solvent[1-3] is entirely understood and taken into account; others, where different observers obtain different moments using the same solvent, must be due to experimental error or impure materials. Too many studies are marked by the extreme scarcity of measurements at really low concentrations. Measurements of the character reported by Hoecker[4] appear much more reliable. A similar survey of dielectric studies of vapors again shows that all too often various workers fail to agree on molecular moments. The author feels that many of these inconsistencies have been introduced likewise through lack of sufficiently extensive data. The present requirement as regards electric moment studies appears definitely one of accuracy and reliability rather than of quantity. With the hope of better fixing some of our moment values, the author, three years ago, obtained data on several alcohol vapors, including the two propyl isomers, and water. The data on water vapor were published.[5] Those on the alcohols have never been reported. At the time the measurements were made, it was believed the alcohols used were of high purity. Shortly thereafter, it was found by Cady and Rarick[6] that the more usual tests of purity often failed to show the presence of appreciable impurities in many of the alcohols. For this reason the author's data were not reported. Recently Cady and Rarick made available to the author some isopropyl alcohol of unquestioned purity, some which they had purified and tested. Dielectric data obtained on this alcohol are presented here.

Dielectric constants were measured by the heterodyne beat method, using previously described apparatus[7] operating entirely on alternating current, along with a carefully calibrated variable capacity standard.[8] The vapor condenser with quartz insulators, and the vapor system, were the same as those used in securing previously reported[5] data on water vapor. Dielectric constants were measured at 12 different temperatures between 26.8°C and 190.4°C. At each temperature, measurements were made at an average of 16 different pressures, ranging from the lowest measurable up to near saturation when such saturated vapor pressure did not exceed one atmosphere. These data are shown in Fig. 1. For the sake of clarity, data are shown for only half of the temperatures used. p'

[1] Müller, Physik. Zeits. **38**, 283 (1937).
[2] Higasi, Inst. Phys. and Chem. Res., Tokyo, Sci. Papers **28**, 284 (1936).
[3] Frank, Proc. Roy. Soc. **152A**, 171 (1935).
[4] Hoecker, J. Chem. Phys. **4**, 431 (1936).
[5] Stranathan, Phys. Rev. **48**, 538 (1935).
[6] Drs. H. P. Cady and Morgan Rarick of the department of chemistry, University of Kansas. Tests of purity were made through accurate and frequent molecular weight determinations during the fractionation. A description of the apparatus will no doubt be published in the near future.
[7] Stranathan, Rev. Sci. Inst. **5**, 334 (1934).
[8] Stranathan, Rev. Sci. Inst. **5**, 315 (1934).

represents the pressure the vapor would exert were it an ideal gas; it is obtained from the observed pressure p and the van der Waals constants a and b, thus:

$$p' = p[1+(p/RT)(a/RT-b)].$$

While obtaining data at so many different pressures at each temperature adds enormously to the experimental data and the associated calculations, the author feels that this is a most desirable procedure. Possibly numerous inconsistent dielectric data in the literature can be attributed to its all too infrequent use. The advantages are threefold: (1) The greater number of points alone should yield a more reliable value for the slope of the curve; (2) Having a well-defined curve allows one to judge much more certainly the extent over which the curve is truly linear. Lack of linearity may result from imperfect correction for deviation from the ideal gas law, and certainly results from adsorption of the vapor on the insulator surfaces[5] in the vapor condenser. The start of such curvature is so gradual that its presence is easily overlooked unless caution is used; (3) The well-defined curve extending to low pressures allows one to evaluate the slope, either graphically or by least squares, without assuming that the curve passes through the origin. The experimental curve may fail to pass through the origin due to any one of the following three causes: Any small error in the zero of the mercury manometer used; failure to correct perfectly for the pressure of the column of liquid, which is not all at the same temperature, present as one builds up the vapor pressure in the test condenser; the possible presence of an effect suggested by Zahn and Miles,[9] due to lack of thermal equilibrium in an evacuated condenser. To the extent that these errors are constant at any one temperature, they will not affect the slope of the curve; hence, it seems unwise to assume that the curve passes through the origin.

The molecular polarization is given by

$$(K-1)M/(K+2)d = (K-1)RT/(K+2)p' = A+B/T,$$

the last equality being a result of the Debye theory. The constant A should be equal to the molecular refraction extrapolated to infinite wave-length; the permanent electric moment of the molecule can be obtained from the constant B. The molecular polarization at any temperature is obtained from the slope of the corresponding curve in Fig. 1. By plotting the data for any temperature to a large scale, one can judge over what pressure range the curve is linear. At higher temperatures, for which the highest pressures used were far below saturation, the entire curve is linear. At the lower temperatures, slight curvature is apparent at the higher pressures. For each temperature the slope of the best least squares line through all points on the linear section was found. The average number of points on these linear sections was 14; in no case were there less than 8. While some personal error of judgment may still enter in determining the extent of the linear section, the least square solution for the slope of this line is no doubt less subject to personal error than is a purely graphical solution.

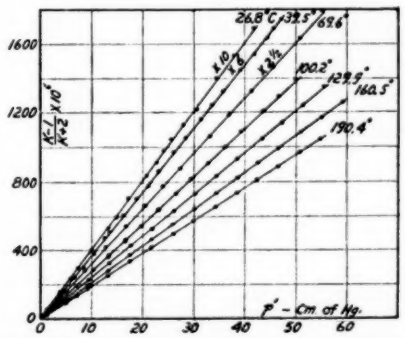

FIG. 1. For the lower temperature curves both ordinate and abscissa have been multiplied by the factor indicated.

Figure 2 shows the products of molecular polarization and absolute temperature plotted against T. The data fall accurately on a straight line, no point being off the line by as much as one percent. Previous data by Kubo,[10] and previous unreported data by the author, are indicated. A least squares solution for the best line through the author's present data gives:

$$(K-1)RT/(K+2)p' = (17.40\pm0.41)+(17{,}490\pm155)/T.$$

This yields an electric moment[11] of (1.682 ± 0.007)

[9] Zahn and Miles, Phys. Rev. **32**, 497 (1928).

[10] Kubo, Inst. Phys. & Chem. Res., Tokyo, Sci. Papers **26**, 242 (1935); **27**, 65 (1935).

[11] This moment is calculated using the Millikan value of e; if the now indicated higher value of e proves correct, then this and all similarly calculated moments will have to be raised by approximately ¾ percent.

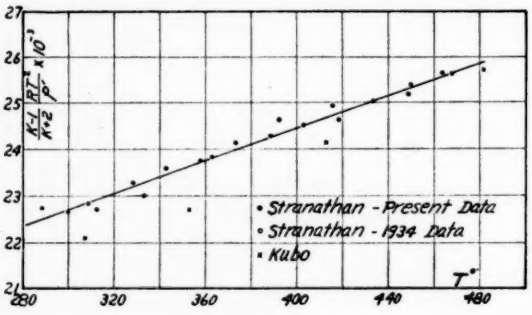

FIG. 2.

$\times 10^{-18}$ e.s.u. for the isopropyl alcohol molecule. The polarization 17.4 contributed by other than the permanent moment is but slightly larger than the electronic molecular refraction, 16.8[10], extrapolated to infinite wave-length; it indicates a smaller atomic polarization than found by Kubo. The electric moment here found does not agree well with previous vapor data. Using data at 4 different temperatures, Kubo found:

$$(K-1)RT/(K+2)p' = 21.1 + 15{,}470/T,$$

yielding a moment 1.58×10^{-18}. On the other hand, the author's present data on undoubtedly pure isopropyl alcohol agree with those obtained but not reported by the author three years ago. At that time the author found, from data at 8 different temperatures ranging from 15.5°C to 194.5°C:

$$(K-1)RT/(K+2)p' = (17.72\pm 0.77) + (17{,}432\pm 295)/T,$$

yielding a moment $(1.679\pm 0.014)\times 10^{-18}$. While the purity of this earlier sample was not the equal of the present, the sample was of the highest grade obtainable, carefully dried and fractionated; it was no doubt the equal of that used by other workers. Several values for the moment of the isopropyl alcohol molecule have been obtained from dilute solution studies. Mahanti[12] reported a value 1.78×10^{-18}; Donle[13] found 1.70; Hennings[14] found 1.63; Mahanti[15] more recently found practically no difference in the moments of various alcohols, giving 1.64 for isopropyl; Higasi[16] reported 1.70, and quotes a value 1.67 obtained from Donle's work. In all of these studies, a common solvent benzene was used; nevertheless, the values are far from consistent. Some are above and some below the present value reported. Ghosh,[17] judging from dilute solution data, concluded that the primary alcohols have practically identical moments, while the iso-alcohols have noticeably higher moments. Groves and Sugden,[18] considering the data of Miles,[19] Knowles,[20] and Kubo,[10] on various alcohol vapors, concluded that there is a small decrease in moment on ascending a homologous series, and a small decrease on passing from a normal to an iso-alcohol; but the authors point out that the effects are not much larger than the experimental error and require further study. Higasi[16] concluded that the moment of an alcohol obtained in solution is always larger than that obtained from vapor measurements. The author feels that most such conclusions regarding the alcohols are far from conclusive until such time as data on both dilute solutions and vapor can be repeated with more consistency than is now apparent.

The author can offer no certain explanation for the discrepancy between Kubo's[10] data and the present data. The difference cannot be attributed to error in calibration. The close agreement of the work of Knowles[20] on ethyl alcohol, the author[5] on water, and unreported work of the author on several alcohols and benzene, with numerous other workers, make it appear impossible that the calibration of apparatus in this laboratory can be appreciably in error. A similar statement can be made regarding many of Kubo's results. Likewise the discrepancy appears rather large to attribute entirely to logical impurities. It is very difficult to separate tert-butyl from isopropyl alcohol by fractional distillation. The boiling point is a very poor test of purity.[6] If a large amount of tert-butyl were present as impurity, it would lead to a higher molecular refraction and probably to a lower moment.[14] The isopropyl used here was definitely pure. The author is convinced that the general procedure followed in the present measurements is a very desirable one; in previous cases, it seems to have led to entirely reliable results.

[12] Mahanti, J. Indian Chem. Soc. **6**, 743 (1929).
[13] Donle, Zeits. f. physik. Chemie Abt. **B14**, 326 (1931).
[14] Hennings, Zeits. f. physik. Chemie Abt. **B28**, 267, 480 (1935).
[15] Mahanti, Zeits. f. Physik **94**, 220 (1935).
[16] Higasi, Inst. Phys. and Chem. Res., Tokyo, Sci. Papers **28**, 284 (1936).
[17] Ghosh, Nature **123**, 413 (1929).
[18] Groves and Sugden, J. Chem. Soc. London, 158, Jan. (1937).
[19] Miles, Phys. Rev. **34**, 964 (1929).
[20] Knowles, J. Phys. Chem. **36**, 2554 (1932).

Transfer of Rotational Energy in Molecular Collisions

II. Exchange of Energy in Collisions Between Unexcited HgH and N_2 Molecules

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It has been found that the intensity distribution in the HgH 4017 band excited by sensitized fluorescence in the mixture $Hg+H_2+N_2$ is influenced by the intensity of the primary light which excites the fluorescence. This observation may be interpreted as evidence of a very slow exchange of vibrational energy in collisions between N_2 and HgH molecules in their normal electronic states. Two other possible causes of the phenomenon—self-reversal and reactions involving high energy Hg atoms formed by stepwise excitation—are ruled out by additional experiments.

I. INTRODUCTION

IN the past few years a great deal of information concerning intermolecular transfers of energy has been derived from experiments on the dispersion of high frequency sound in gases. Of particular interest is the discovery that in a few cases the cross section for exchange of energy between vibration and translation is tens of thousands of times smaller than the gas-kinetic cross section. However, no case has been discovered in which the exchange of rotational energy is slow enough to cause dispersion of sound at even the highest frequencies used in the experiments.

Another approach to the problem of transfers of energy in collisions is the study of intensity distributions in band spectra, which give detailed information about the distribution of molecules among rotational and vibrational levels. It is often found that the intensity distribution shows a pressure dependence, and the effect of collisions may be studied by following the intensity distribution as a function of the pressure of the emitting gas or of an added foreign gas. If, as is usual, it is the emission spectrum on which the observations are made, the collisions which are most effective in modifying the intensity distribution are those that occur during the brief interval ($\sim 10^{-8}$ sec.) during which the molecule occupies an excited electronic state.[1]

Experiments of this type, in which the spectrum studied was that of HgH excited by sensitized fluorescence and the foreign gases were water vapor and nitrogen, have been described in a previous paper.[2] It was found that both H_2O and N_2 are effective in altering the rotational distribution of the excited HgH molecule. Because of the fact that the dependence of intensity distribution on pressure is caused primarily by collisions which occur while the HgH is in an excited state, it is difficult to obtain from the pressure variations any information about the exchanges of energy which occur when the molecule is in the normal electronic state. The following considerations suggested that for this purpose it would be worth while to carry out further experiments on the sensitized fluorescence in which the intensity distribution in the HgH spectrum is studied as a function of the intensity of the primary Hg 2537 radiation which excites the fluorescence.

The HgH bands appear when the mixture (1/1000 mm Hg vapor+a few 1/1000's mm H_2 +a few mm N_2) is irradiated with the unreversed 2537 resonance line of Hg.[3] The HgH molecules are formed in the reaction

$$Hg'+H_2 \rightarrow HgH+H$$

and are excited by a collision of the second kind

$$Hg'+HgH \rightarrow Hg+HgH',$$[4]

(Hg' denotes a metastable (6^3P_0) Hg atom).

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[1] For a bibliography and critical discussion of the general field of transfers of energy in collisions the reader is referred to a review by Oldenberg and Frost, Chem. Rev. **20**, 99 (1937).

[2] F. F. Rieke, J. Chem. Phys. **4**, 513 (1936).

[3] E. Gaviola and R. W. Wood, Phil. Mag. **6**, 1191 (1928).

[4] H. Beutler and E. Rabinowitch, Zeits. f. physik. Chemie **B8**, 403 (1930).

The intensity distribution in the spectrum shows that a considerable proportion of the excited HgH molecules have rotational energy greatly in excess of the thermal value. Because of the selection rule for the rotational quantum number, the rotational energy is not changed appreciably by the emission process which restores the molecule to the normal electronic state. The spectrum (reference 2, Fig. 7) shows also that many excited molecules reach the normal electronic state by a transition to the vibrational level $v=1$.

Let us now assume that there is an appreciable probability that a molecule which has an excess internal energy (of rotation or vibration) immediately after the radiation process may retain the energy until it is re-excited by an encounter with a metastable Hg atom. It is reasonable to assume that the energy level to which such a molecule is excited in a collision of the second kind is different than for a molecule which has only the thermal energy. Whether or not the conditions are favorable for such a retention of internal energy should then have an influence on the intensity distribution in the emission spectrum.

The probability P that the excess internal energy be lost in the interval between the radiation process and the following excitation process is determined by the ratio $R=\sigma_1^2[N_2]/\sigma_2^2[Hg']$ where σ_1^2 is the cross section for loss of energy in a collision with an N_2 molecule, σ_2^2 the cross section for a collision of the second kind with metastable mercury, and $[N_2]$ and $[Hg']$ are partial pressures. If all other conditions remain constant, $[Hg']$ is directly proportional to I, the intensity of the primary radiation; in this case P is a function of I only. Consequently the intensity distribution in the fluorescence spectrum should depend on the intensity of primary radiation; but for the effect to be appreciable it is necessary that R be of the order of magnitude of 1. This can happen only in case σ_1^2/σ_2^2 is of the order of magnitude of 10^{-5}, for even under the best conditions $[Hg']$ is of the order of 10^{-5} mm,[5] while $[N_2]$ is a few mm.[6]

[5] H. Beutler and E. Rabinowitch, Zeits. f. physik. Chemie **B6**, 233 (1929).

[6] The argument of these two paragraphs was suggested by, and is somewhat similar to, parts of reference 4. Beutler and Rabinowitch were concerned with the possibility that abnormal rotation resulting from the chemical reaction in which the HgH is formed (reaction of metastable mercury with H_2 and with H_2O) might persist until a subsequent excitation process and thus influence the emission spectrum. However, the experiments described in reference 2 prove that the abnormal rotation contributed by the formation process is negligible compared to that which results from the excitation process and collisions which occur during the lifetime of the excited state. The present paper is concerned with a persistence from one excitation process to the next; the number of collisions which intervene is estimated from the considerations advanced by Beutler and Rabinowitch

Although the ratio $[N_2]/[Hg']$ can also be influenced by varying the pressure of N_2, the relation is not simple; furthermore the average number of collisions during the lifetime of the excited state of HgH is also dependent on the pressure of N_2. Consequently experiments in which only the exciting intensity is varied are most suitable for studying the exchange of energy in collisions between the unexcited HgH and N_2 molecules.

II. Experimental Results and Their Interpretation

(1) Persistence of internal energy between consecutive excitation processes

Photographs of the HgH bands excited by sensitized fluorescence were taken, following the procedure described previously.[2] Then wire gauzes were inserted between the Hg arcs and the fluorescence tube, in order to reduce the illumination of the latter by a known ratio, and additional exposures were taken. Two pairs of wire gauzes were used; one pair had a transmission of about $\frac{1}{2}$; the other, $\frac{1}{5}$. The first experiment was performed with H_2 and N_2 in the fluorescence tube. Photometry of the photographic plate resulted in a definite indication that the intensity of the high rotation lines, relative to the low rotation lines, in the 4017 band[7] decreased with the intensity of the primary radiation.

The exposure times necessary for obtaining comparable spectra varied approximately as the inverse square of the exciting intensity, as had been observed by Gaviola and Wood.[3] Independent trials had been made to determine the relation between exposure time and the proper-

[7] This is the only band which is sufficiently intense and free from overlapping to permit quantitative measurements with low dispersion apparatus.

ties of the photographic plates which were used.

Nevertheless, since the difference in intensity distribution observed in the first experiment was not very large, the experiment was repeated in such a way as to eliminate the possibility of any error arising from uncertainty in the correction for different exposure times. For one of the exposures made with the full intensity of primary light, a wire gauze was placed over the lens used to project the fluorescence radiation onto the slit of the spectrograph and a long exposure made. Comparison could then be made between spectra of similar densities for which the exposure times were equal. The result of the previous experiment was confirmed. The observations are given in detail in Table I; values of t/h given in the table indicate the intensity of the tail (high rotation lines) relative to the head (low rotation lines).

The HgH bands can also be excited if the fluorescence tube contains a few mm of water vapor instead of the H_2+N_2 mixture, but the relative intensity of the high rotation lines is much less.[3] The intensity distribution in the 4017 band excited with 3.6 mm of water vapor in the fluorescence tube did now show any variation with the intensity of the primary radiation.

The observation of a dependence of the intensity distribution on the intensity of the primary radiation for the 4017 band excited in H_2+N_2 is consistent with the assumption that the exchange of either vibrational or rotational energy in collisions between normal HgH and N_2 molecules is very slow. But before the agreement may be taken as evidence of the persistence of energy in collisions, some alternative interpretations must be taken into account.

(2) Discussion of alternative explanations

One possibility is that the observed dependence of intensity distribution on the exciting intensity might be caused by strong self-reversal of the 4017 band (the "resonance band" of HgH) within the fluorescence tube. Oldenberg's experiments with OH show that even though the emission spectrum shows abnormal rotation, the absorption is confined to the low rotation lines.[8] If similar conditions held in the fluorescence tube, self-reversal would influence the intensity of the band head only. Reducing the intensity of the primary radiation decreases the concentration of HgH, consequently at low intensities the band head should appear with its full intensity; in other words, the intensity of the tail relative to the head should decrease when the intensity of the primary radiation is decreased. This is just the effect observed.

[8] O. Oldenberg, Phys. Rev. **46**, 210 (1934).

TABLE I. *Observed intensity distributions in the 4017 band of HgH.*

p_{H_2}	p_{N_2}	Exciting Intensity	Intensity Distribution (i/h)
0.007 mm	2.8 mm	1.0	0.43
		0.5	0.27
		0.2	0.22
.007	6.0	1.0	0.76
		0.2	0.42

In order to test for this source of error, the following experiment was performed. In the fluorescence tube used for the preceding experiments, the depth of the region in which the fluorescence is excited is only three cm., but there is an additional path of eight cm to the exit window. An appreciable concentration of HgH should imply a rather long life and therefore diffusion into this space. This argument suggested the construction of a fluorescence tube in which the fluorescence could be observed from either end of the tube; in one direction the maximum absorbing path was two cm; in the opposite direction a path of fifteen cm was possible. It seems reasonable that if there is any appreciable absorption, it would be greater for spectra taken through the more distant window. However, spectra taken from either end under otherwise identical conditions were very similar. Therefore it may be concluded that the amount of self-reversal is negligible, and that all of the observed intensity distributions are determined by the population ratios of the various rotational levels.

The possibility remained that in the case of intense illumination molecules with abnormal rotation might be excited largely as a result of the presence of Hg atoms in the 6^3P_2 or higher states. Since the filter does not transmit the 1849 line, any atoms of excitation higher than

the $^3P_1$ state can occur only as a result of stepwise excitation, and their concentration must vary as a higher power of the exciting intensity. Since the ratio $6^3P_2/6^3P_0$, for instance, increases with the intensity of exciting radiation[9] (of constant energy distribution), the effect of exciting intensity on the intensity distribution in the HgH bands might be explained by the variation in the above ratio. But in that case a corresponding change in intensity distribution should occur when the ratio is varied by changing only the intensity of the higher series Hg lines in the primary radiation. Consequently the following experiment was made.

One exposure, with 0.01 mm H_2+5 mm N_2, was made with the fluorescence tube illuminated by one of the water-cooled, magnetically-deflected mercury arcs. A second exposure was made with the fluorescence tube illuminated by both the low temperature arc and another arc run at a high pressure. The 2537 line emitted by the high pressure arc is strongly reversed, and is not absorbed by the cool Hg vapor in the fluorescence tube, but the higher series lines are only slightly reversed in the arc, and can be absorbed by the excited Hg atoms in the fluorescence tube. The rate of excitation of 6^3P_1 Hg atoms, and therefore of 6^3P_0 atoms, was approximately the same for both exposures, but the rate of excitation of higher states was many times greater for the second exposure. Nevertheless, there was no indication of a difference in the intensity distribution in the HgH 4017 band. This result proves that the high rotation lines observed in the sensitized fluorescence experiments cannot be attributed to any process involving Hg atoms in the 6^3P_2 or higher states. The foregoing conclusion is also supported by the observation that with H_2O (instead of H_2 +N_2) in the fluorescence tube, the intensity distribution in the 4017 band is independent of the exciting intensity.

(3) Conclusions

Since both of the alternative hypotheses are inconsistent with the additional experimental evidence, we conclude that the first explanation of the relation between intensity distribution and exciting intensity, based on the persistence of internal energy in collisions, is correct. We may now attempt to decide whether it is a persistence of rotational or of vibrational energy which occurs.

In a preliminary report[10] it was suggested that the experiments indicate that it is the rotation which persists, since it is the distribution among rotational quanta which was observed to depend on the primary intensity. This conclusion is open to the following objections. Firstly, evidence obtained from the dispersion of sound experiments uniformly indicate a good exchange of energy between rotation and translation. Secondly, by analogy with transfers of vibrational energy, a persistence is to be expected only in case the quanta involved are large compared to kT;[11] but the rotational quanta of HgH are at most (for $J=30\frac{1}{2}$) only equal to kT.

In subsequent discussions, Professor J. Franck has pointed out that the observations may be interpreted to be a consequence of the persistence of vibration, rather than of rotation. It is necessary to assume only that in the collision of the second kind,

$$\mathrm{Hg}'+\mathrm{HgH}\rightarrow\mathrm{Hg}+\mathrm{HgH}',$$

the probability that the HgH be excited to a high vibrational level ($v=4$ or 5) is greatly enhanced if the molecule is originally in the first, rather than the zero, vibrational level. This assumption is supported by the Franck-Condon principle applied to the potential curves of HgH derived by Rydberg.[12] In this case, the increased rotation observed with high exciting intensities is to be explained as an indirect result of an enhanced proportion of molecules excited to the levels $v=4$ or $v=5$ of the $^2\Pi$ state, for it has been shown previously that molecules in these levels are transferred by collisions with N_2 molecules to the high rotation levels of the $v=0$ level.

The foregoing, which appears to be the most plausible interpretation of the experiments, leads to the conclusion that collisions with N_2 have a very small effective cross section for the removal of the last quantum of vibration from the HgH molecule in the normal electronic state, although only a very rough estimate of the actual cross

[9] E. Gaviola, Phil. Mag. **6**, 1154 (1928).

[10] F. F. Rieke, Phys. Rev. **47**, 788(A) (1935).
[11] Reference 1, p. 118.
[12] R. Rydberg, Zeits. f. Physik **80**, 514 (1933).

section can be made. As shown in Section I of this paper, an effect of the kind observed should occur only in case the cross section for loss of the final quantum of vibration is of the order of magnitude of 10^{-5} times the cross section for the collision of the second kind with metastable Hg. The latter cross section may be comparable to the gas kinetic cross section, or even somewhat larger, but it is very unlikely that it is larger by a factor as great as 10^2. This rough argument indicates that the cross section in question is of the same order of magnitude as some of the smaller cross sections found for similar processes by the dispersion of sound method.

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The Effect of Concentration on the Production of the Latent Photographic Image by Hydrogen Peroxide

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Much of the density previously reported as produced by short immersions of photographic plates in aqueous solutions of hydrogen peroxide was found to have been produced during the washing interval between exposure and development. Data are presented concerning the production of the latent image by various concentrations of hydrogen peroxide. Analysis of this data suggests that, initially, the net reaction is of the second order. An optimum concentration for the production of maximum density was indicated.

MANY substances have been reported as producing latent images when placed near or in contact with photographic emulsions. Radioactivity, phosphorescence and thermal fogging furnish satisfactory explanations in many cases. In many others, the action is due to the presence or formation of at least traces of hydrogen peroxide.[1] For this reason and because of its own intrinsic interest, especially its bearing on the problem of the mechanism of latent image formation, the fogging action of hydrogen peroxide has been the subject of much investigation.

In practically all the early work,[2–4] photographic plates were exposed to hydrogen peroxide vapor. In previously reported work where plates were immersed in aqueous solutions of hydrogen peroxide,[5, 6] they were washed for 30 minutes before development. We find that much of the density observed was produced during this washing period. Among other studies employing this technique, Sheppard and Wightman[5] made some tests with the same time of immersion for different concentrations and concluded that the effect of increasing concentration was similar to that of increasing light intensity. Further investigation along somewhat similar lines, but substituting a 1–2 second rinse for the 30 minute washing interval, has been carried out in this laboratory. Plates so briefly rinsed inevitably carry along some hydrogen peroxide into the developer. However, in agreement with observations of Wightman, Trivelli and Sheppard,[7] tests showed that negligibly little additional density was produced by the presence of small quantities of hydrogen peroxide in the developer.

The first group of tests was performed with ten concentrations ranging by geometrical progression from 3 percent to 3/512 percent and immersions, also in geometrical progression, from 1 second to 128 seconds. Portions of Eastman "33" plates were immersed for measured intervals in hydrogen peroxide of a given concentration, rinsed 1–2 seconds in water, developed 5 minutes in a pyro-soda formula, rinsed in 1 percent

[1] Keenan, Chem. Rev. **3**, 95 (1926).
[2] Russell, Proc. Roy. Soc. London **64**, 409 (1899).
[3] Dony-Henault, O. and A., Bull. Soc. Chim. Belg. **22**, 224 (1908).
[4] Dombrowsky, Inaug. Dissert., Leipzig (1908).
[5] Sheppard and Wightman, J. Frank. Inst. **195**, 337 (1923).
[6] Jones and Blair, J. Frank. Inst. **218**, 29 (1934).
[7] Wightman, Trivelli and Sheppard, J. Frank. Inst. **200**, 335 (1925).

acetic acid, fixed, washed and dried in the usual manner. Operations were carried out at 21°C.

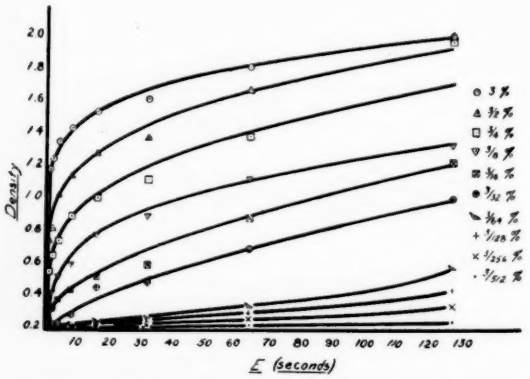

FIG. 1. Early stages of the process, showing the growth of developable density with time of exposure (immersion) in aqueous hydrogen peroxide of the stated concentrations.

The densities produced have been plotted against time of exposure (immersion) in Fig. 1.

The slopes of the density-time of exposure curves were determined from Fig. 1 at densities of 0.3, 0.4, 0.6, 0.8 and 1.0. The logarithms of these slopes were then plotted as a function of the logarithm of the concentration of hydrogen peroxide. For each density, straight lines were drawn following the trends of points thus determined. The slopes of these latter lines, interpreted as the order of the net reaction, were found to be 1.74, 1.56, 1.41, 1.14 and 0.97, respectively, for the densities in increasing order as mentioned above. Extrapolation of these results back to the density, 0.2 of a fixed-out, unexposed plate suggests that the reaction is initially of the second order. The decrease of the apparent order of the net reaction with increasing density is probably due, in part at least, to a reverse reaction causing developable grains to become undevelopable. Presumably the process is complicated by the conditions of diffusion of the hydrogen peroxide into and within the emulsion and its adsorption thereby. Dombrowsky,[4] it may be noted, found a definite tendency toward surface images when plates were exposed to hydrogen peroxide vapor for short intervals.

Other tests were carried on to solarization, i.e., until maximum density had been attained for the particular concentration and immersions for still longer intervals began to yield decreasing densities. The results are presented in Fig. 2 from which it is evident that the intermediate concentration of $\frac{3}{8}$ percent hydrogen peroxide produced a higher maximum density than either extreme, 3 percent or 3/512 percent. Another series of observations was then made to determine the maximum developable densities produced by each of the same ten concentrations with which Fig. 1 is concerned. The fact that plates of different emulsion number were used in all three of these series of tests minimizes the significance of too close, direct comparison, as has been emphasized in a previous paper.[6] However, the magnitude of the maximum density attained was found to increase, with

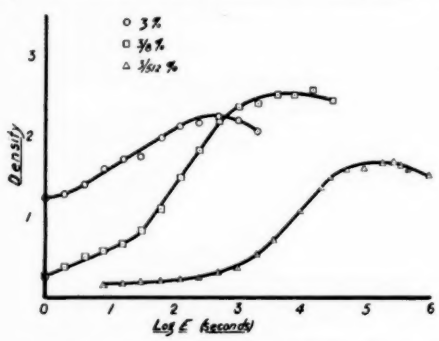

FIG. 2. Full range of exposure showing beginning of solarization and indicating an optimum concentration for the production of maximum density. Densities are plotted against logarithms of exposures (immersions).

increasing concentration, from 1.5 with 3/512 percent hydrogen peroxide up to 3.0 with the $\frac{3}{4}$ percent solution. Beyond this, it began to decrease with further increase of concentration, thus confirming the implication of Fig. 2 that there is an optimum concentration for the production of the latent photographic image by hydrogen peroxide in aqueous solution.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Supraconductivity in Aromatic Compounds

The abnormally large values of the diamagnetic anisotropy of bismuth, graphite and particularly of the aromatic compounds have already led to the hypothesis[1] that in these substances the diamagnetic currents might not be restricted, as usually, to the individual atoms but might circulate from one atom to the other along orbits of considerable length, e.g., along the aromatic rings. To this hypothesis I have recently given a theoretical basis, developing a theory which may be considered as the extension of the so-called "molecular orbital theory" to the case of the presence of a magnetic field.[2] It could be shown why these *interatomic currents* are essentially *restricted to the aromatic ring-systems* and why they cannot appear in the interior of saturated molecules nor, as intermolecular currents, between saturated molecules.[3] If one considers only interactions between neighboring atoms, the wave equation for the single electronic wave function c_k and energy E can be written in the form (the index k denotes the different aromatic C atoms):

$$\sum_l c_k[\eta_{kl} W_1 e^{2\pi i f_{kl}} + \delta_{kl}(W_0 - E)] = 0. \qquad (1)$$

Here

$$\eta_{kl} = \begin{cases} 1 \text{ if } k \text{ is a neighbor of } l \\ 0 \text{ if } k \text{ is not a neighbor of } l \end{cases} \qquad \delta_{kl} = \begin{cases} 1 \text{ if } k = l \\ 0 \text{ if } k \neq l \end{cases}$$

W_1 is the ordinary exchange integral of neighbors of the orbital theory,

W_0 is the coulombian integral,

$f_{kl} = (e/hc)HS_{kl}$ where H is the external magnetic field and S_{kl} is the area of the triangle formed by the neighbors k, l and a zero point, arbitrarily chosen in the plane of the molecule.

We consider the distances between neighboring aromatic C atoms as equal, so that we have to deal with only one value W_1 for the exchange integral.

By means of Eq. (1) I have calculated[3] the relative anisotropies $\Delta\chi$ of the diamagnetic susceptibility for various aromatic molecules, taking the anisotropy of benzene as unit. The results are listed in Table I, together with the experimental values given by Lonsdale[4] ($\Delta\chi_{\text{benz.}} = 54 \cdot 10^{-6}$). Our calculation makes no use of any adjustable parameter; the theoretical values of the second column are a direct consequence of Eq. (1). If one wants to obtain the ex-

TABLE I. *Relative diamagnetic anisotropies* ($\Delta\chi/\Delta\chi_{\text{benz.}}$)

	$(\Delta\chi/\Delta\chi_{\text{benz.}})$ exper.	$(\Delta\chi/\Delta\chi_{\text{benz.}})$ theor.	$(\Delta\chi/\Delta\chi_{\text{benz.}})$ semi-class.
Naphthalene $C_{10}H_8$	2.11	2.18	2.40
Anthracene $C_{14}H_{10}$	3.38	3.45	3.88
Phenanthrene $C_{14}H_{10}$	3.07	3.04	3.88
Pyrene $C_{16}H_{10}$	4.32	4.46	6.92
Diphenyl $C_{12}H_{10}$	2.20	2.21	2.00

perimental *absolute* value $\Delta\chi_{\text{benz.}}=54\cdot10^{-6}$ for the anisotropy of benzene with a C−C distance of 1.39A, the exchange integral W_1 must have the value

$$W_1=4.4\ [e\cdot\text{volts}].$$

About a year ago, in a paper published in this journal, Pauling[1] tried to calculate the diamagnetic anisotropies of aromatic compounds, taking as a basis the hypothesis that in these compounds the "aromatic" electrons can freely circulate around the aromatic rings. We can represent Pauling's calculus in a very simple way stating that *the aromatic compounds shall behave like supraconductors*, i.e., that for any cyclic way in the molecule the following equation[5] holds:

$$\lambda\oint i_s ds=-\int\int H_n d\sigma \quad (i=\text{intensity of current}). \quad (2)$$

Applying this equation to any cyclic way and postulating in addition the conservation of electricity at any ramification, one obtains just as many relations as necessary for unambiguously calculating the distribution of current. The constant λ must have the value

$$\lambda=1.12\cdot10^{-6}\ [\text{sec./cm}]$$

if one wants to obtain the experimental value $\Delta\chi_{\text{benz.}}=54\cdot10^{-6}$ for the anisotropy of benzene, assuming an effective area of $5\cdot10^{-16}$ cm² for the hexagon of that molecule.

The theory characterized by (2) can be considered as a kind of "semi-classical" analog of (1), insofar as it could be shown[3] that for the limiting case of cyclic molecules of an *infinite* number of atoms, the two theories become identical. But for the real aromatic molecules this limiting case is very far from being realized. That is clearly demonstrated by the values listed in Table I under "semi-classical," which show great deviations from the experimental values as well as from the theoretical ones.

In order to make up for these deficiencies Pauling introduces a series of corrections which he attributes to variations of the electronic density and of the curvature and length of the links in the different aromatic compounds. I could not comprehend why all these effects should have such a great influence upon the susceptibility, as assumed by Pauling, and I thought it reasonable to consider none of them for a preliminary discussion. Accordingly in Table I the *uncorrected* values of both theories are compared. The application of corrections like those considered by Pauling seems to me scarcely compatible with the actual exactitude not only of the theoretical calculations but also of the measurements.

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September 4, 1937.

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[2] F. London, Comptes rendus **205**, 28 (1937).
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[4] K. Lonsdale, Proc. Roy. Soc. **A159**, 149 (1937).
[5] F. and H. London, Physica **2**, 341 (1935), Eqs. (8) (9).